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METHODS FOR THE RAPID AND ACCURATE MEASUREMENT OF NITRATE AND SULFATE IN ATMOSPHERIC PARTICULATES

D. Williams, et al

Abcor, Incorporated

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16. Abstracts The objectives of this study were as follows: to develop rapid and accurate analytical methods for the determination of nitrate and sulfate in atmospheric particulate samples; to compare the new methods developed with current spectrophotometric methods for nitrate and sulfate. An Orion nitrate electrode is used to measure nitrate leached from High Volume filter samples. A known amount of silver fluoride is added to the extract, and a fluoride electrode is used as the reference. The silver ion precipitates possible interferences of the nitrate electrode (Cl^-, B^-r, I^-, VO_3^-, $SeO_4^=$). A sulfate procedure was developed using a lead precipitation teachnique and measuring the excess lead ion with an Orion lead electrode. Increased sensitivity was obtained by adding an equal volume of methyl cellosolve acetate (MCA) to the High Volume filter extracts. Studies on leaching the sulfate or nitrate from the High Volume filter samples were performed. The techniques and results are reported. The nitrate method is a direct method and is also procedurally very simple. No interferences are anticipated. The sulfate methods measures sulfate only, and is procedurally more difficult than the nitrate method. The recommended procedures for nitrate and sulfate analysis are appended to this report.

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APPENDIX B - RECOMMENDED PROCEDURE FOR SULFATE ANALYSIS

REFERENCES

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I. SUMMARY AND RECOMMENDATIONS

A. PROJECT OBJECTIVES

1. To develop rapid and accurate analytical methods for the determination of nitrate and sulfate in atmospheric particulate samples.

2. To compare the new methods developed with current spectrophotometric methods for nitrate and sulfate.

B. SUMMARY

Ion selective electrodes are used for the measurement of nitrate and sulfate leached from high volume filter samples. The nitrate method uses a direct measurement with a nitrate electrode. The sulfate method uses a lead ion precipitation of sulfate, and a lead ion-selective electrode.

1. Nitrate Procedure

An Orion nitrate electrode is used to measure nitrate leached from High Volume filter samples. A known amount of silver fluoride is added to the extract, and a fluoride electrode is used as the reference. The silver ion precipitates possible interferences of the nitrate electrode (Cl^-, Br^-, I^-, VO_3^-, $SeO_4^=$). It is believed that bromide is the most probable interference of this electrode in these samples.

In the experimental evaluation of this method, nitrate was leached from 48 cm^2 strips of filters. The filter pulp need not be removed, and as little as 10 ml of H_2O can be used using an ultrasonic bath. However, for comparison with colorimetric methods the filter was leached with 25 ml H_2O and the filter pulp removed. A calibration curve method was found to be preferable to the standard addition method. Statistical analysis of random nitrate standards shows that this calibration curve method is accurate to ±10% (C.V.) from 3×10^{-5} molar to 10^{-3} molar, and presumably higher. The standard deviation in this analysis was ±2.0 millivolts. Greater precision should be possible since other investigators using a similar nitrate electrode have obtained a 0.36% C.V. with a flow system and temperature control. Since the response of the electrode

is logarithmic (56 mv/decade a broad concentration range of extracts can be assayed without dilution. In 15 ml, the range from 3×10^{-5} to 10^{-3} molar covers nitrate from 28 µg to 930 µg.

Ten filter strips were analyzed for nitrate by the electrode, Sawicki and Scaringelli, and phenol disulfonic acid (PDS) methods. Recovery of added nitrate was also determined by each of these methods. One sample was outside the range of the Sawicki method. One of the remaining samples gave an electrode value which was 70% high. For the remaining samples we obtained a good correlation with both methods ($r = 0.986$ and 0.945). Also, the slopes of the regression lines were 1.0 ±10%. Standard deviations between the methods for these samples were 13% (Electrode-Sawicki) and 22% (Electrode-PDS).

2. Sulfate Procedure

A sulfate procedure was developed using a lead precipitation technique and measuring the excess lead ion with an Orion lead electrode. Increased sensitivity was obtained by adding an equal volume of methyl cellosolve® acetate (MCA) to the High Volume filter extracts. In this mixed solvent the solubility of $PbSO_4$ is lowered several orders of magnitude. Methods of measuring the excess lead included simple potentiometric titration, determination of equivalency by extrapolation of Gran's plots, and calculation of excess lead using a standard subtraction method. Although the other methods appeared promising the standard subtraction method was found to be most reliable. Lead solutions of relative concentrations (0.3, 1, 3, 10, etc.) were chosen such that no less than 30% of the lead should be precipitated. At this point the relative error per mv is 19%. It decreases rapidly, being 8% mv at 50% precipitation, and 2% mv at 80% precipitation.

In a study of random order sulfate standards a standard deviation of 1.5 mv was obtained. In this test, quantities from 0.04 to 4 mg of sulfate were added in 5 ml of aqueous solution.

Nine filter sections were analyzed for sulfate by the electrode and barium chloranilate procedures. The methods agreed for seven of the samples ($r = 0.992$, $y = 0.945x + 0.039$) for sulfate from 0.65 to 0.225 mg (5% of extract).

The percent standard deviation for these samples was 10%. The remaining two samples were from Birmingham, Alabama. The electrode gave higher values and we hypothesize that metal ions may have decreased the chloranilate values.

3. General Conclusions

The nitrate method is the most direct method we know of for nitrate analysis. It is also procedurally very simple. No interferences are anticipated. However, because of the logarithmic electrode response, precision is achieved with some difficulty (4%/mv). With recently developed electrodes, and careful handling, this limitation should be unimportant.

The sulfate method measures soluble sulfate only, and is procedurally more difficult than the nitrate method. With the procedure presented in the recommendations section, however, the method would be simpler than other soluble sulfate procedures. This is especially true if an ion exchange step is required for the chloranilate procedure. The precision of the sulfate procedure can be improved by using more lead standards (this study used two per decade). A good correlation with the chloranilate method was obtained for most samples. The question of interference in the remaining samples remains to be resolved.

C. RECOMMENDATIONS

1. Nitrate

A larger number of filter sections should be analyzed by the electrode method, and compared to the two colorimetric methods. A statistical analysis should be performed to test if the methods are identical, and also to determine the precision of the electrode method. If the methods are not identical a study of the interferences of each method should be undertaken.

The nitrate method can be further simplified by leaching with AgF solution. This method is presently used with the nitrate monitor under development in EPA Contract No. 68-02-0591. Limited comparison of the methods indicates no differences. A smaller quantity of solution should be used with a specially constructed solution holder.

Nitrate precision should be improved by careful attention to electrode upkeep, solution temperature and stirring. Also, newer Orion nitrate electrodes may improve the precision of the method.

2. Sulfate

a. Determination of Discrepancy of Methods for Samples from Birmingham, Alabama (S-7, S-9)

This task takes priority because if the electrode method is in error on these samples, then the method may require major modification to eliminate the interference. (We believe adding an ion exchange step to the chloranilate procedure will result in equivalent responses for the electrode and colorimetric assays).

We would recommend the duplicate analysis of a large number of filter samples by the electrode method, and a comparison to both the chloranilate and thorin procedures.

b. Simplification of the Procedure

The method, as developed in the present program and recommended in the Appendix, uses an aliquot of filtrate and adds an equal volume of MCA. If a 50/50 MCA/H_2O solution can be used for leaching, then an unmeasured volume of filtrate can be used for analysis. Furthermore, a smaller volume and therefore more concentrated sulfate sample can be obtained in this manner. Calculations can be made on the mv deflection of a small sample which will indicate whether more sample or blank should be added. This will allow a decade response from one lead solution.

c. Titration Method

Although a titration method was not successful in the early stages of this investigation, with the use of MCA and with proper instrumentation this method should yield accurate results. For electrode stability we would recommend adding SO_4 = to an initial excess of Pb^{++}. With an automatic titrator (with differentiator, if necessary) the time to reach equivalence could be correlated to the sulfate level in the sample.

If this concept is valid we would recommend that this procedure be extended to include continuous titration from a Leap Sampler washed with 50% MCA in water.

II. INTRODUCTION

A. BACKGROUND

Sulfate and nitrate in particulate matter are clearly important constituents since these species represent about 12% and 3% by weight of the total suspended particulate matter in the ambient air. Furthermore, the sulfate and nitrate in particulates are presumably the products of oxidation of sulfur and nitrogen oxides, which are of importance as gaseous pollutants. A summary of data from the National Air Sampling Network (NASN) is given in Table I. Note the small (factor of 2) range in concentration between the arithmetic average for the urban and non-urban values, and also the standard deviation of values from a particular site (Tables II & III). Since sulfate is to be determined by addition of excess lead, its modest standard deviation indicates that the analyst can usually use the correct lead concentration the first time.

The methods in use by NASN for NO_3^- and $SO_4^=$ involves aqueous extraction of 10% of the high volume filter and subsequent wet chemical analysis. The technique for sulfate is the methyl thymol blue method and a Technicon auto-analyzer is required. The nitrate method involves reduction to NO_2^-, and then determination by a colorimetric diazotization (Saltzman) method. Both methods are time consuming and involve addition of a number of reagents and require considerable calculations. Hence, we have attempted to develop a more rapid and simplified procedure. These methods employ ion selective electrodes. The method is direct for nitrate (nitrate electrode) and indirect for sulfate (lead electrode). The direct measurement of nitrate is expected to have minimum interferences. The sulfate measurement by lead sulfate precipitation is similar in concept to the barium precipitation methods now in use, and will have the same general interferences. In these cases only soluble sulfate is measured.

In order to determine the required sensitivity needed for an analytical method, we can calculate the volume of air sampled with a 24-hour high volume sampler. If we assume a sampling rate of 566 liter/min.for 24 hours, we obtain a total volume of 815 m^3 (see Table IV). For a non-urban

TABLE I

SUMMARY OF DATA FROM NASN AND CONTRIBUTING
STATE AND LOCAL NETWORKS
(Values in $\mu g/m^3$)

Pollutant	Urban			Non-Urban		
	No. of Stations	Arith. Average	Max. Station Average	No. of Stations	Arith. Average	Max. Station Average
Suspended Particulates	217	102	254	30	38	79
Nitrates	132	2.9	13.5	29	1.3	2.5
Sulfates	132	10.7	28.8	29	5.6	12.6
Nitrogen Dioxide	47	141	333			
Sulfur Dioxide	45	62	346			

TABLE II

SULFATES, NON-URBAN FREQUENCY DISTRIBUTIONS

State / Station	Years	Number of Samples	Micrograms Per Cubic Meter													Std Geo Dev
			Min	Frequency Distribution - Percent									Max	Arith Mean	Geo Mean	
				10	20	30	40	50	60	70	80	90				
ARIZONA GRAND CANYON PK	65	24	1.2	1.4	1.7	1.8	1.9	1.9	2.0	2.2	4.5	5.8	6.3	2.2	2.1	1.36
CALIFORNIA HUMBOLDT COUNTY	65	24	1.8	2.1	2.4	2.6	3.0	3.4	3.7	4.2	4.5	5.9	7.6	3.7	3.5	1.47
COLORADO MONTEZUMA COUNTY	65	23	.9	.9	1.6	2.1	2.3	2.4	2.8	3.0	3.4	3.7	4.0	2.5	2.3	1.54
DELAWARE KENT COUNTY	65	23	4.0	4.9	6.5	7.0	7.7	8.9	9.8	10.2	11.1	14.1	25.7	9.5	8.7	1.51
FLORIDA FLORIDA KEYS	64	21	2.3	2.2	2.4	2.7	2.9	3.2	3.8	4.8	5.3	5.9	9.9	3.9	3.8	1.47
GEORGIA DUTTE COUNTY	65	23	1.1	1.4	1.8	1.9	2.0	2.2	2.3	2.5	2.7	3.7	4.3	2.4	2.3	1.38
ILLINOIS PARKE COUNTY	65	25	1.3	4.5	6.2	6.7	7.0	7.5	7.9	8.4	9.4	13.4	14.8	8.0	7.3	1.63
IOWA DELAWARE COUNTY	65	25	1.0	2.5	3.2	4.2	4.7	5.1	6.2	6.7	7.0	8.6	10.7	5.3	4.7	1.68
MAINE ACADIA NAT PARK	65	22	1.8	2.0	2.6	3.0	3.8	4.5	6.2	7.3	12.9	14.3	16.9	6.7	5.9	2.09
MARYLAND CALVERT COUNTY	65	26	5.9	5.8	6.8	7.8	8.3	9.4	12.0	14.1	16.1	19.7	28.8	11.6	10.4	1.61
MISSISSIPPI JACKSON COUNTY	65	25	2.0	3.9	4.2	4.8	5.3	5.7	5.9	6.6	7.3	8.1	8.4	5.7	5.5	1.38
MISSOURI SHANNON COUNTY	65	26	2.8	3.4	3.8	4.2	4.4	4.9	5.5	6.0	6.9	7.7	10.0	5.3	5.0	1.38
MONTANA GLACIER NAT PARK	65	23	2.2	2.3	2.6	2.8	2.9	3.1	3.4	3.8	4.3	4.9	5.1	3.4	3.3	1.30
NEBRASKA THOMAS COUNTY	65	26	2.1	2.4	2.7	3.0	3.1	3.4	3.7	3.9	4.3	4.5	5.9	3.5	3.4	1.29
NEVADA WHITE PINE CO	65	23	2.2	2.5	2.9	3.1	3.3	3.5	3.8	3.7	4.0	4.5	8.5	3.8	3.6	1.36
NEW HAMPSHIRE COOS COUNTY	65	23	1.8	2.5	3.4	3.8	4.5	5.5	5.8	6.2	8.9	12.0	17.1	6.1	5.2	1.74
NEW MEXICO RIO ARRIBA COUNTY	65	25	.7	1.2	1.4	1.8	1.9	2.2	2.5	2.9	3.1	3.8	5.4	2.4	2.1	1.61
NEW YORK CAPE VINCENT	65	25	3.6	4.0	4.5	6.6	7.3	9.4	12.0	13.3	14.1	18.2	24.8	10.0	8.7	1.76
NORTH CAROLINA CAPE HATTERAS	65	25	4.4	2.7	5.3	6.8	8.6	9.8	10.2	11.1	14.7	16.7	21.0	9.2	7.8	1.92
OKLAHOMA CHEROKEE COUNTY	65	26	1.6	1.9	2.1	2.3	2.6	3.2	3.7	4.0	4.8	5.3	17.7	4.3	3.4	1.85
OREGON CURRY COUNTY	65	24	1.3	1.9	2.5	2.8	3.0	3.1	3.2	4.0	4.3	8.0	10.3	3.8	3.4	1.62
PENNSYLVANIA CLARION COUNTY	65	25	1.7	3.8	4.8	6.8	7.6	8.3	9.1	11.1	13.1	16.7	19.2	9.0	7.8	1.78
RHODE ISLAND WASHINGTON CO	65	26	3.9	4.5	5.0	6.2	6.6	7.1	10.8	12.0	15.4	16.7	90.0	12.6	9.1	2.00

TABLE III

NITRATES, NON-URBAN FREQUENCY DISTRIBUTIONS

County, State or Station	Years	Number of Samples	Micrograms Per Cubic Meter												Std Geo Dev
			Min	Frequency Distribution - Percent									Max	Arith Mean	Geo Mean	
				5	10	20	30	40	50	60	70	80				
ARIZONA GRAND CANYON PK	65	24	.1	.2	.3	.3	.4	.4	.4	.5	.5	.8	1.3	.5	.4	1.69
CALIFORNIA HUMBOLDT COUNTY	65	24	.1	.2	.3	.4	.5	.6	.6	.9	.9	1.2	1.5	.7	.6	1.86
COLORADO MONTEZUMA COUNTY	65	23		.1	.1	.2	.2	.2	.3	.3	.4	.5	1.0	.3	.3	1.92
DELAWARE KENT COUNTY	65	24	.8	1.0	1.5	1.6	2.0	2.3	2.6	2.9	3.1	3.4	3.6	2.3	2.1	1.54
FLORIDA FLORIDA KEYS	64	21	.1	.2	.3	.3	.4	.5	.6	.8	1.0	1.4	1.6	.7	.6	2.02
IDAHO BUTTE COUNTY	65	23	.1	.1	.2	.2	.2	.3	.3	.4	.5	.7	1.8	.4	.3	1.98
NEVADA PARKE COUNTY	65	25	.2	1.0	1.1	1.2	1.3	2.0	2.3	2.8	3.4	3.8	4.4	2.1	1.8	1.97
OHIO DELAWARE COUNTY	65	25	.2	.4	.7	.9	1.2	1.8	1.9	2.2	2.6	3.0	3.7	1.7	1.3	2.13
MAINE ACADIA NAT PARK	65	22	.2	.2	.3	.4	.6	.8	.9	1.0	1.6	1.9	2.9	.9	.7	2.12
MARYLAND CALVERT COUNTY	65	26	.3	1.1	1.2	1.3	1.3	1.4	2.2	2.3	2.7	2.8	3.1	1.8	1.6	1.75
MISSISSIPPI JACKSON COUNTY	65	25	.5	1.0	1.1	1.3	1.5	1.6	1.7	2.1	2.3	3.7	8.1	2.0	1.7	1.79
MISSOURI SHANNON COUNTY	65	26	.6	.8	1.0	1.3	1.4	1.6	1.9	2.3	2.5	3.0	3.2	1.8	1.6	1.64
MONTANA GLACIER NAT PARK	65	23	.1		.1	.1	.1	.1	.2	.2	.2	.3	.6	.2	.2	1.70
NEBRASKA THOMAS COUNTY	65	26	.2	.2	.2	.3	.5	.6	.7	.8	.9	1.0	2.3	.7	.6	1.93
NEVADA WHITE PINE CO	65	23	.1	.1	.1	.2	.2	.3	.3	.4	.5	.6	1.0	.4	.3	1.86
NEW HAMPSHIRE COOS COUNTY	65	23	.2	.3	.5	.5	.6	.7	.8	1.0	1.4	2.3	3.6	1.1	.8	2.07
NEW MEXICO RIO ARRIBA COUNTY	65	25	.1	.1	.1	.2	.2	.2	.3	.3	.4	.5	.7	.3	.3	1.73
NEW YORK CAPE VINCENT	65	25	.4	.6	.8	1.3	2.0	2.4	2.8	3.5	3.8	4.4	4.9	2.5	1.9	2.18
NORTH CAROLINA CAPE HATTERAS	65	25	.4	.6	.6	.9	1.1	1.4	1.7	1.9	2.6	2.4	8.8	1.9	1.5	2.00
OKLAHOMA CHEROKEE COUNTY	65	26	.1	.4	.6	.7	.8	.8	.9	1.0	1.3	1.7	3.2	1.0	.9	1.97
OREGON CURRY COUNTY	65	24	.1		.1	.2	.3	.3	.3	.4	.4	.5	.8	.3	.3	1.91
PENNSYLVANIA CLARION COUNTY	65	25	.3	.5	.9	1.3	1.4	1.6	1.9	2.0	2.7	3.7	4.1	1.8	1.5	2.04
RHODE ISLAND WASHINGTON CO	65	26	.7	.9	1.1	1.4	1.7	1.9	2.0	2.9	3.7	4.2	6.8	2.5	2.1	1.84

TABLE IV

REQUIRED SENSITIVITIES FOR $SO_4^=$ AND NO_3^-

$$\text{Total Volume } (m^3) = \frac{20\ ft^3/min \times 60\ min/hr \times 24\ hrs \times 28.3\ l/ft^3}{1000\ l/m^3} = 815\ m^3$$

The weight (total) of NO_3^- and $SO_4^=$ is as follows:

NO_3^- = 1.3 $\mu g/m^3$ x 815 m^3 = 1.06 mg or 0.106 mg for 10% of sample

$SO_4^=$ = 5.6 $\mu g/m^3$ x 815 m^3 = 4.56 mg or 0.456 mg for 10% of sample

If the sample (above) is dissolved in 10 ml of solution, the concentration is:

NO_3^- = 1.4×10^{-4} moles/liter

$SO_4^=$ = 5.8×10^{-4} moles/liter

---

atmosphere, we take average NO_3^- and $SO_4^=$ values of 1.3 and 5.6 $\mu g/m^3$, respectively. The weights of $SO_4^=$ values and NO_3^- are given for both the total filter sample and 10% of the sample. If we assume 10% of the sample is taken and dissolved in 10 ml of solution, this gives us a measure of the sensitivity required for the average sample. The detection limit should probably be 1/10 of these values.

The range for the nitrate electrode is 10^{-1} to 10^{-5} M and for the lead electrode is 10^{-1} to 10^{-7} M according to the manufacturer's literature.

B. NITRATE MEASUREMENT

The nitrate electrode is linear over > four orders of magnitude. Thus, any concentration range desired can be measured without dilution of the sample. A list of interferences for the Orion liquid ion exchange electrode is given in Table V. For this electrode (the k value for NO_3^- = 1.0). ClO_4^- gives 1000 times the nitrate response for an equal concentration. Perchlorate, I^-, $S^=$, Br^-, ClO_3^- are not expected to be significant interferences since these species are not present at high concentrations in the atmosphere. Chloride ion which can be present in high concentrations in sea coast areas has a selectivity constant of 4×10^{-3}. Thus, with an equimolar mixture of nitrate and chloride, the potential (mv value) due to chloride would be 0.4% that of nitrate. We see that the effect of chloride is quite small. Similar considerations apply to the other known possible interfering anions.

C. SULFATE MEASUREMENT

Since there is no ion selective electrode commercially available for sulfate, our effort has been placed on using the lead electrode and measuring the excess lead after $PbSO_4$ precipitation. This procedure has been described in Orion literature (Orion 94-82A). The sample, in 50% methanol, is titrated with lead perchlorate, and the electrode potential is monitored throughout the titration with a millivolt meter. The endpoint is determined by plotting ml of titrant added versus the electrode potential. The major difficulty with the potentiometric titration is that nearly 20-25 points are needed to obtain an accurate curve.

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TABLE V

ANIONIC INTERFERENCES AND THEIR SELECTIVITY COEFFICIENTS FOR THE NITRATE ELECTRODE

Approximate Anion Selectivity Constants			
Interfering Ions	K_x	Interfering Ions	K_x
ClO_4^-	10^3	Cl^-	4×10^{-3}
I^-	20	OAc^-	4×10^{-4}
ClO_3^-	2	$CO_3^=$	2×10^{-4}
Br^-	1.3×10^{-1}	$PO_4^=$	1×10^{-4}
HS^-	4×10^{-2}	F^-	6×10^{-5}
NO_2^-	4×10^{-2}	$H_2PO_4^-$	5×10^{-5}
CN^-	1×10^{-2}	$SO_4^=$	3×10^{-5}
HCO_3^-	9×10^{-3}	$HPO_4^=$	3×10^{-5}

An alternate method of assimilating data is the use of Gran's plots. These plots involve plotting ml of titrant vs potential (mv) on semi-antilog paper which is designed to accommodate the volume change which occurs during the titration. The basis for this selection of axes is Nernst's equation:

$$E = E^{o} + \frac{RT}{nF} \log [A^{-}]$$

Rearrangement yields:

$$\frac{nFE}{RT} = \frac{nFE^{o}}{RT} + \log [A^{-}]$$

The ion sensed can be made a linear function of the electrode potential by taking the antilog of both sides:

$$\text{antilog } (E/S) = E_1 + [A^{-}]$$

where $S = nF/RT$ and $E_1 = \text{antilog } (E^{o}/S)$.

The change in volume is corrected for by shifting the axis up 10% from left to right making additions of up to 10% of the original sample volume possible. Gran's plot paper has a slope of 58 mv for a monovalent electrode and 29 mv for a divalent electrode. Corrections for electrodes whose slopes differ from 58 mv can be achieved by the use of a blank.

There are two major advantages to the use of Gran's plot paper. Since the plot is linear, fewer points (4-6) are needed and the time per determination is reduced considerably. A straight line is drawn through the points and the endpoint is found by extrapolation to the x axis. Secondly, this method is well suited for small amounts of sulfate, since points well beyond the endpoint can be used to obtain the straight line and hence the endpoint, thus eliminating the difficulties encountered with electrode instability.

A third technique involves addition of sulfate to an excess of lead and determination of the difference in potential (mv). The reduction in potential between the initial lead solution and the solution containing

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sulfate is a direct measure of the sulfate content. The advantage of this technique is the rapidity of the determination. It also has the advantage that a direct reading sulfate meter could be constructed.

The interferences in the lead electrode are given in Table VI below.

TABLE VI

INTERFERENCES IN THE SOLID STATE LEAD ELECTRODE

Hg, Ag, Cu	Must be absent
Fe, Cd	No interference unless the concentration is greater than that of lead

The "interference" for the lead electrode involves a poisoning of the electrode surface. PbS is the active matrix of the electrode and has a K_{sp} of 10^{-26}. Any element which as a $K_{sp} < 10^{-26}$, e.g., CuS, HgS, AgS, will "poison" the electrode. Thus, these metals must be absent from the solution. CdS and Fe_2S_3 have about the same K_{sp} as PbS. Therefore, Cd and Fe can be tolerated in high concentrations. Sulfide ion is an example of an anion which poisons the Pb^{++} electrode. We have, however, used the lead electrode in solutions from a kraft mill which had high concentrations of $S^{=}$. Good results were obtained, but the electrode had to be cleaned frequently.

In order to determine the applicability of the electrode for sulfate determination in atmospheric Hi Vol samples, the interfering metals which might be present must be considered further. In Table VII, we have taken data from NASN (1968) for New York City which is one of the most extreme cases, and calculated the average concentrations of various "problem metals" and compared them to the average sulfate levels present in the city. Silver is not present in the ambient air and presents no potential problem. Little, if any, mercury is collected on the Hi Vol filter

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TABLE VII

COMPARISON OF SULFATE AND METAL ION CONCENTRATIONS FOR NEW YORK CITY

	$\mu g/m^3$ (N.Y.C.)	Conc. (M/l)*	$M/SO_4^=$
Ag	NA		
Hg	NA		
Cu	0.3	$< 4 \times 10^{-5}$†	0.013
Pb	1.6	$< 6 \times 10^{-5}$†	0.020
Fe	2.3	$< 4 \times 10^{-4}$†	0.10
Cd	0.069	$< 6 \times 10^{-4}$†	0.002
$SO_4^=$	30	3×10^{-3}M	

*Assume Hi Vol sample 815 m^3

10% of sample taken and dissolved in 10 ml

†Note the assumption is made that all of the metal salts are soluble; this is not true but these concentrations represent the maximum attainable values.

(Thompson, 1972). The concentration of copper, however, is quite significant, $\leq 1\%$ of the $SO_4^{=}$ level. It is unlikely that much of the copper dissolves in the aqueous solution, however, since most of the copper is present as CuO which has a low solubility in aqueous solutions. However, even a small amount of Cu could be a problem over the long term. If the electrode must be polished too often, a copper complex forming agent could be added to the solution. Amine complexes of copper should remove this possible interference, if this is necessary.

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III. PRELIMINARY STUDIES

Some preliminary studies were performed on particulate samples collected in Cambridge, Mass. by Hi Vol samplers placed near Walden. Filters #1 and 2 represent two different Hi Vol samples collected over a 24-hour period. Filters #3 and 4 were collected at a later date but also represent two Hi Vol samples run side by side.

The first two filters were collected just after a rainstorm. The prevailing winds were off the ocean. The latter two samples were collected with the wind in an easterly direction, off the land.

The 8"x 10" Hi Vol sample papers were divided into 10 equal areas and cut into strips using a razor blade and straight edge. Nitrate and soluble sulfate were leached from the strips (10% of the area) with approximately 25 ml of boiling water. The samples were cooled to room temperature, the liquid was decanted into a 50 ml volumetric flask and the filter paper residue was rinsed several times with distilled water. The volumetric flask containing the sample was then diluted to volume (50 ml) with water. Note that no filtration step is necessary since the electrodes can measure the potential in turbid solutions with no loss in accuracy. This is one inherent advantage of electrode methods over spectrophotometric techniques.

The nitrate, chloride, iodide, and copper results were determined by direct potentiometric measurement with ion selective electrodes. The chloride determinations were checked by potentiometric titration with standardized Ag^+ solution. The titration was monitored with an ion selective silver electrode. The Cl^- electrode and Ag^+ titration results agreed to within approximately 5%. The sulfate measurements were made by titration with standard $Pb(ClO_4)_2$ in a 50% alcohol-50% aqueous solution. The progress of the titration was determined with a Pb electrode.

The nitrate electrode measurements on the filter samples yielded the results in Table VIII. These values are in good agreement with the NO_3^- levels in urban areas. Since halides may interfere with the nitrate electrode determination, and no levels were readily found in the literature,

TABLE VIII

ANALYSIS OF SUSPENDED PARTICULATE MATTER IN CAMBRIDGE AIR WITH ION SELECTIVE ELECTRODES

Filter No.	Species Concentration $\mu g/m^3$						Remarks
	Total Particulate	NO_3^-	$SO_4^=$	Cl^-	I^-	Cu^{++}	
1	57.6	4.7	0.3	23.2	BD	BD	Wind blowing off ocean (from the east)
2	54.4	3.6	0.3	38.8	BD	BD	
3	59.3	4.7	11.3	4.2	BD	BD	Light westerly winds
4	53.4	4.4	11.6	3.1	BD	BD	

BD = below detectable by electrode - $< 10^{6}$ M/l I^-, $< 10^{-5}$ M/l Cu^{++}

the concentrations of Cl^- and I^- were also measured. The Cl^-/NO_3^- concentration ratio for filters #1 and 2 is approximately 15. This concentration of Cl^- presents no error in the nitrate measurement. These filters probably represent one of the worst cases encountered for halide interferences. The wind was directly off the ocean for filters #1 and 2. This is confirmed by the extremely low $SO_4^=$ values. $SO_4^=$ levels approximately 1 $\mu g/m^3$ or less are typical of non-urban areas. However, no major sources of SO_2 were present between the ocean and the sampling site. No I^- was detected in the samples. A sea water sample was collected and analyzed. The Cl^-/I^- ratio measured was 3.6×10^5. On this basis, the I^- levels from sea spray would be approximately two orders of magnitude below the detectable level of the I^- electrode. Although I^- has a selectivity constant of 20, the low levels present in the atmospheric samples indicate no interference. No Br^- measurements were made but Cl^-/Br^- measurements of particulate samples collected over the ocean indicate a ratio of approximately 200-500. For filters #1 and 2, the predicted Br^- concentrations are more than an order of magnitude less than the NO_3^- levels. With a selectivity coefficient of 0.3, Br^- does not appear to be a problem from salt spray.

Filters #3 and 4 are more typical air samples. These values show approximately the same NO_3^- levels but the Cl^- (sea salt aerosol) is decreased by an order of magnitude.

The sulfate measurements (potentiometric titration with the Pb electrode as a monitor) in filters #1 and 2 are nearly at the limit of the method. The titrant was 10^{-3}M $Pb(ClO_4)_2$ standardized against H_2SO_4. Filters #3 and 4 are more representative and typical of urban $SO_4^=$ levels. No problems were encountered with the titration at this level. Copper ion is an interference for the Pb electrode, therefore soluble copper measurements were made for these filter extracts. As expected, no soluble copper was found in these samples.

Lininger, et al. (1966) collected atmospheric particulate samples (Cambridge, Mass.) in a cascade impactor. The material on the first three stages was combined and determined by neutron activation analysis. The halogen concentration ranges found for Cambridge, Mass. are given below:

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Cl^-	Br^-	I^-
$\mu g/m^3$	ng/m^3	ng/m^3
1-6	20-200	2-10

Note that the Cl^- levels are approximately the same as samples #3 and 4 in Table VIII.

The halide/nitrate ratios using Lininger's halogen values and our measured NO_3^- data are 1, 0.025, and 0.001 for Cl^-, Br^- and I^-, respectively. If we consider the halide selectivity coefficients for the nitrate electrode, we find that the percent interference for Cl^- ($k = 6 \times 10^{-3}$) and I^- ($k = 20$) is essentially zero because of the high rejection of the electrode for Cl^- and the very low concentration of I^- in the atmosphere. The Br^- ($k = 0.13$) interference, however, is perhaps measurable and may account for as much as 0.3% error if all the Br^- were soluble.

In a second study, ten Hi Vol samples were collected in Leominster and Natick, Massachusetts. These sites are approximately 35 miles from the ocean. Hence, the halide/NO_3^- ratios for non-coastal areas were observed. The data are presented in Table IX. Most of the samples were non-urban. The high value for filter #9 is due to its close vicinity to a heavily traveled gravel area. Note that NO_3^-, $SO_4^=$, Cl^- and Pb in this sample are low. The high suspended particulate level is, therefore, due mainly to dust. The low value in sample #7 is the result of a site which is distant from any automotive or other type of pollutant emissions. No analytical problems were encountered with these levels of NO_3^- or $SO_4^=$ with the electrodes.

The Br^-/NO_3^- ratio for samples 5-10 would give an average 2% error in the measurement with the nitrate electrode (assuming $Br^- = 0.13$, and $NO_3^- = 1$ for the electrode). A 6% average error would be expected on the basis of the Br^-/NO_3^- ratios observed in samples 11-14. This indicates that bromide removal is necessary since the interference with the NO_3^- measurements could be significant. Statistical analysis of samples 5-14 gives the results below in Table X.

TABLE IX

SUSPENDED PARTICULATE SAMPLES FROM THE LEOMINSTER-FITCHBURG AND NATICK AREAS

Site	Filter No.	Concentration ($\mu gm/m^3$)						
		Suspended Particulate	NO_3^-	$SO_4^=$	Cl^-	Br^-	I^-	Pb (dithizone)
Leominster, Mass.	5	39.5[a]	0.77	1.42	1.58	0.09	BD	0.53
	6	58.4[b]	0.87	1.47	0.54	0.18	BD	1.73
	7	15.6[b]	0.76	0.26	0.28	0.07	BD	0.28
	8	37.4[b]	1.74	2.15	0.20	0.17	BD	0.21
	9	91.3[b,c]	0.86	0.86	0.10	0.18	BD	1.07
	10	45.2[b]	0.78	0.57	0.10	0.10	BD	0.58
Natick, Mass.	11	19.64	0.84	1.38	0.30	0.41	BD	1.11
	12	34.75	0.66	0.57	0.21	0.32	BD	0.87
	13	57.2	0.64	1.02	0.05	0.13	BD	0.54
	14	101.1	1.12	0.44	0.38	0.63	BD	2.90

(a) urban

(b) non-urban

(c) near heavily traveled gravel area

TABLE X

Species Correlated	Correlation Coefficient
Pb vs Br^-	0.82
Cl vs Br^-	0.13
Suspended particulate vs Pb	0.69
Suspended particulate vs NO_3^-	0.11

This analysis shows that the particulate is automotive related, as is the source of bromide (high correlation between suspended particulate and Pb, also Pb and Br).

IV. LEACHING STUDIES

The primary step in the determination will involve leaching the $SO_4^=$ or NO_3^- from the filter sample. This can be done by percolating an aqueous solution through the filter or by dissolving the anions directly into the aqueous solution to be used for analysis.

Many analytical methods require only a minimal amount of sample. The sensitivity of a method can therefore be improved if the filter is leached with a lesser amount of water, thus increasing the ion concentration.

For any leaching method, it is necessary that all of the leachable sample be dissolved. However, it is not necessary that all of the leached sample be recovered. In our experiments we found that the limiting volume of solution was determined by the amount of filter pulp which could be suspended and shaken in the container. The best sample container for effective removal of the leaching solution was a test tube. A filter press could be used with this system and only 0.3 ml of solution remained in the pulp of a 7-inch^2 (45 cm^2) piece of filter. However, because of bumping, this system could not be used with a boiling technique.

Using electrodes for measurement, it is possible that the filter need not be removed. However, for our later studies, comparing colorimetric and electrode methods the filter was removed.

In an early test using the nitrate electrode, the filter was not removed and the system was leached for 5 minutes. This data was compared to values obtained as the solution reached boiling, and again after 2 hours boiling. These data are shown as Series 1 in Table XI. Ten different measurements were made on sections of two Hi Vol filters.

A more comprehensive leaching study was then undertaken for both nitrate and sulfate. The colorimetric methods of analysis were used to determine the efficacy of the leaching methods. The filter strip (2.5 cm x 17.8 cm) was rolled with gloves on and placed in a 16 mm test tube. Ten or 15 ml of distilled water were added at time zero and the filter was broken up using a clean metal spatula. It was found necessary to leach the filter presses

TABLE XI

NITRATE LEACHING STUDIES
(Values in μg)

Series I: Averages of Ten Sections of Filter Analyzed Consecutively; Filter Left in Solution

5 min after immersion	at boiling point	after 2 hr boiling
640	750	740

Series II: Four Sections of Filter; Comparison of Broken and Whole Sections by Two Leaching Methods

Leaching Method	Broken	Not Broken
30 min, 90°C	129	118
30 min, 25°C	200	160

Series III: Comparison of Eight Leaching Methods Arranged by Rank

Time (min)	Agitation	Temp. (°C)	NO_3^-	(No. of Tests)
10	None	25	106	(1)
30	None	90	126	(2)
30	None	25	150	(2)
10	Shaking table	25	192	(2)
30	Shaking table	25	235	(2)
30	Ultrasonic	25	240	(2)
10	Ultrasonic	25	350	(1)
120	None	100	370	(1)

with dilute HCl before use. At the specified time, these presses were inserted with a slow twisting motion into 16 mm test tubes and the clear solution decanted from the stem of the press (Filter/Sampler, Unichem, P5190-6, Scientific Products, McGraw Park, Ill.).

In the initial study, 15 ml of distilled water were used and some filters were not broken up with the spatula. Comparison of similar leaching methods indicated that breaking up of the filter was advisable (Table XI, Series II). Comparison of the 10 and 15 ml tests indicated no improvement due to increased fluid volume.

Table XI, Series 3 shows the results of filter samples broken with the spatula. Ten and 15 ml leaching samples are averaged. The samples for each leaching method were initially chosen at random. For the second group the same order was maintained, but the strips were offset by five -- placing the previous end sections in the middle. We found no effect of position on the amount of material leached out. The filters were 24-hour high volume filter samples taken at Walden during the winter.

A similar study was performed on leaching of sulfate, using the barium chloranilate procedure. These data are shown in Table XII.

From the data of these studies, it is evident that the ultrasonic bath is very effective in solubilizing the sulfate. The nitrate studies are less conclusive. However, we currently believe the ultrasonic method to be a viable alternative to heating.

TABLE XII

SULFATE LEACHING STUDY

Six Leaching Methods Arranged by Rank (μg)			
Time (min)	Agitation	Temp. (°C)	$SO_4^=$ Concentration
30	None	90	670
30	Shaking Table	R.T.	758
10	Shaking table	R.T.	1495
120	None	100	1496
10	Ultrasonic	R.T.	1517
30	Ultrasonic	R.T.	1539

V. NITRATE ELECTRODE METHOD

The method developed for measurement of nitrate in this program is a direct measurement, using an Orion ion-selective nitrate electrode. Since the method is direct, there are a minimum number of possible interferences. The non-specificity of the electrode, however, does generate possible positive errors. These we have attempted to eliminate by addition of complexing agents. Milham (1970) and Milham, et al. (1970) describe nitrate analyses of plants and soils using an Orion nitrate electrode. They also use a solution which includes silver ion in order to reduce interferences. These investigators report a limit of sensitivity which is similar to our tests. They also indicate an excellent coefficient of variation (C.V. = 1.5%). With a flow system and temperature control, they indicate a 0.36 (C.V.) for standards and 0.63% (C.V.) for plant extracts. Hence, we believe that this method should provide a useful method for analysis of nitrate in air pollution samples.

A. ALTERNATE METHODS OF NITRATE ANALYSIS

Although the measurement of nitrate with the nitrate specific ion electrode is direct and has minimum interferences, a method with increased sensitivity would be advantageous.

Alternate methods of ion selective electrode measurement of nitrate include reduction of the nitrate, and measurement of nitrite or ammonia.

An electrode which responds to nitrite has been briefly investigated at Orion. However, it was not sufficiently developed to warrant evaluation in this program. If it were to be used, reduction of nitrate to nitrite could be required. This could be accomplished by the methods presently used to produce nitrite in the colorimetric diazotization procedures for the measurement of nitrate. The method would measure nitrate and nitrite, unless a blank were run without the reduction step.

The ammonia electrode is commercially available and appears to be more sensitive than the nitrate electrode. This may be due to the lack of interferences, since the electrode employs a gas barrier. The electrode

has been used for the measurement of nitrate using a reduction by aluminum powder. The method is described in the Orion instruction manual for the ammonia electrode. The method does not give complete conversion of nitrate to ammonia, but this might be improved by using an active metal reducing agent (Zn) in a column (M. Frant, Orion, personal communication). The method includes several steps (acidification with HCl and NaF, addition of aluminum, and addition of NaOH to release NH_3).

Obviously, the ammonia electrode will measure ammonium and nitrite, plus nitrate. Removal of endogenous ammonium might be accomplished by prior addition of base. However, this would make the method difficult and time consuming. The endogenous ammonium concentration is comparable to the nitrate concentration in air pollution samples.

We therefore preferred to develop the nitrate measurement using the nitrate electrode method but reducing the sample size by reducing the leaching volume. If necessary, the volume could be further reduced by evaporation, followed by the electrode method using a small volume in a microcell or flow-through cell configuration. Such cells are commercially available from Orion.

B. EVALUATION OF INTERFERENCES

The major interferences appear to be from the response of the electrode to halides. However, the response to metal oxide anions such as selenate and vanadate were also studied.

1. Evaluation of Halide Interferences

Iodide, which would be the major halide interference with the nitrate electrode, was not found in any of the extracted Hi Vol filters. Bromide, which is an interference with the nitrate electrode, although less of one than iodide, was found in the extracted samples. Chloride, although present in the extracted samples, is not a major interference with the nitrate electrode. In any case, however, silver fluoride addition has been found to eliminate any of these halide interferences, if and when they exist in the extracted samples.

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a. Determination of the Selectivity Constant for Bromide

The selectivity constant indicates the nitrate electrode error when bromide is present in extracted samples. The selectivity constant of the nitrate electrode for bromide was determined using potassium nitrate standards and three different bromide concentrations (4×10^{-3}, 4×10^{-4}, and 4×10^{-5}M NaBr). A 25 ml aliquot of each nitrate standard with 1 ml of known concentration of bromide was run. The millivolt readings were plotted (Figure 1) and the selectivity constant was determined at each concentration of bromide. The selectivity constant can be related to the activity (concentration) of the interfering ion by the equation:

$$A_x = K_i A_i^{Z/Z_i}$$

where: Z = charge on ion being measured - $Z = -1$ for NO_3^-

Z_i = charge on interfering ion - $Z_i = -1$ for Br^-

A_x = concentration (activity) of ion being measured

A_i = concentration of interfering ion

K_i = selectivity constant for the interfering ion

A_x is determined from the plotted curve by extrapolating the Nernstian response part of the curve and the plateau part of the curve. The point on this curve where ΔE is $\frac{18}{Z}$ mv from the extrapolated Nernstian response line gives a value for A which is equal to A_x (Orion Newsletter, 1969). K_i can then be calculated from this information. The experimental selectivity constants with bromide as the interfering anion were found to be:

$K = 0.3$ @ 4×10^{-5}M Br^-

$K = 0.18$ @ 4×10^{-4}M Br^-

$K = 0.17$ @ 4×10^{-3}M Br^-

The average is $K = 0.21$. The reported selectivity constant of the nitrate electrode for bromide is $K = 0.13$ (Orion Manual, 1971). The observed discrepancy between the experimental and reported values is not unexpected.

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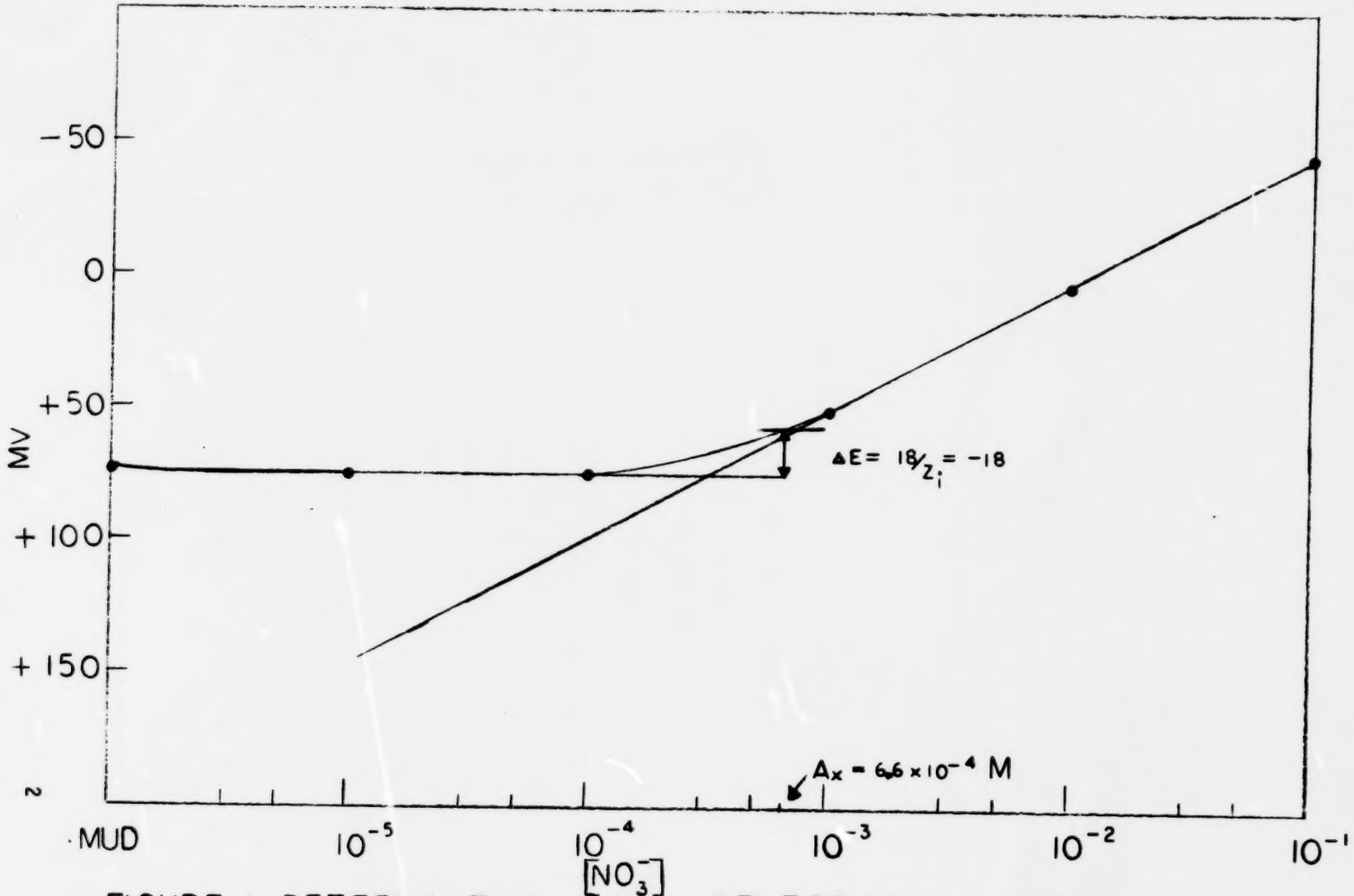

FIGURE 1 DETERMINATION OF SELECTIVITY CONSTANT

It is reported that K_i's calculated this way could vary by as much as a factor of two depending on the particular electrode and the level of the background interference (Orion Newsletter, 1971).

b. Removal of Interferences from Nitrate Measurement by AgF Addition

Bromide, chloride, iodide, and several other potential interferences are precipitated by silver ion. This precipitation is sufficient to remove the electrode interferences, without filtration of the precipitant.

Silver fluoride was chosen as the silver salt to be added since fluoride is not a significant interference, and the salt is readily soluble.

The fluoride electrode was investigated as the reference for the nitrate electrode since an excess of F^- will be added to the solution. The use of a solid state electrode eliminates the liquid junction potential commonly associated with liquid reference electrodes. We ran some comparisons of nitrate determinations using the calomel and fluoride reference electrodes. The data for four different days are given in Table XIII. It appears that the slope is closer to Nernstian and the detection limit is improved with fluoride addition and fluoride reference electrodes.

It should be noted that Milham (1970) also used Ag^+ to remove interferences, and Manahan (1970) used the fluoride electrode as a reference electrode for the determination of nitrate with an Orion nitrate electrode.

c. Demonstration of Bromide Interference Removal Using AgF

To demonstrate the removal of bromide interference, the nitrate electrode was used with the fluoride electrode as the reference. The millivolt reading of a 25 ml aliquot of each nitrate standard with 1 ml of 10^{-1}M AgF added was first taken. A second millivolt reading was taken after the addition of 1 ml of 10^{-2}M Br^- to each solution of standard

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TABLE XIII

COMPARISON OF FLUORIDE AND CALOMEL ELECTRODES AS REFERENCE ELECTRODES FOR THE NITRATE SELECTIVE ION ELECTRODE

	9/27/72		9/28/72		9/29/72		10/2/72	
Concentration KNO_3	(a) mv	(b) mv with AgF Addition	(a) mv	(b) mv with AgF Addition	(a) mv	(b) mv with AgF Addition	(a) mv	(b) mv with AgF Addition
Mud (no KNO_3)		+319	+278	+314	+286	+324	+290	+331
10^{-6}			+261	+317	+252	+309	+284	+330
2.5×10^{-6}							+279	+327
5×10^{-6}					+270	+309	+276	+325
7.5×10^{-6}					+267	+309	+271	+319
10^{-5}	+257	+277	+261	+306	+269	+313	+268	+318
2.5×10^{-5}					+240	+300	+250	+301
5×10^{-5}					+263	+284	+235	+289
7.5×10^{-5}					+260	+276	+226	+280
10^{-4}	+215	+264	+214	+269	+219	+269	+217	+270
2.5×10^{-4}			+194	+245	+197	+246		
5×10^{-4}			+178	+227	+180	+229		
7.5×10^{-4}			+168	+217	+170	+219		
10^{-3}	+156	+210	+160	+210	+163	+212	+162	+211
10^{-2}	+103	+153	+108	+151	+107	+154	+106	+151
10^{-1}	+ 53	+ 96	+ 58	+ 96	+ 53	+ 98	+ 55	+ 95
slope (mv/decade) 10^{-4}M-10^{-2}M)	+ 56	+ 55.5	+ 53	+ 59	+ 56	+ 61	+ 55.5	+ 59.5

(a) Nitrate electrode and fiber tip calomel reference electrode
(b) Nitrate electrode and fluoride electrode as reference electrode

and silver. The curves obtained were identical (Figure 2), thus indicating that the bromide interference is removed by the silver ion addition, and that the electrode system is indeed responding to the nitrate concentration relative to the fluoride ion concentration.

2. Effect of Selenate on the Nitrate Electrode

The effect of the presence of selenate on the measurement of nitrate concentration was also investigated. The presence of selenium as an atmospheric contaminant originates with the incineration of paper, the coloring of paints and inks, the production of glass and plastics, and the refining of copper, lead, and zinc. Since selenium often acts like a non-metal, we investigated its effect on the response of the nitrate electrode. It was found that the interference of selenium would be minimal. The data are presented in Figure 3 as apparent nitrate at various selenium to nitrate ratios.

3. Effect of Vanadate on the Nitrate Electrode

The effect of the presence of vanadate on the measurement of nitrate concentration was also investigated. It was found that at high concentrations, vanadium appears to affect the nitrate concentration measurement by lowering the millivolt readings of the nitrate standards (Figure 4). This experiment was performed by addition of different amounts of a 10^{-1}M sodium orthovanadate solution to nitrate standards.

It should be noted that the normal leveling effect of an interference does not occur until the nitrate concentration is down to 10^{-5}M. At this point, the vanadate concentration is an order of magnitude higher than the nitrate concentration.

4. Removal of Selenium and Vanadium as Interferences with the Nitrate Electrode

The effect of selenium and vanadium on the nitrate electrode using the nitrate-fluoride electrode system with silver fluoride addition was investigated after the development of this system. As reported above,

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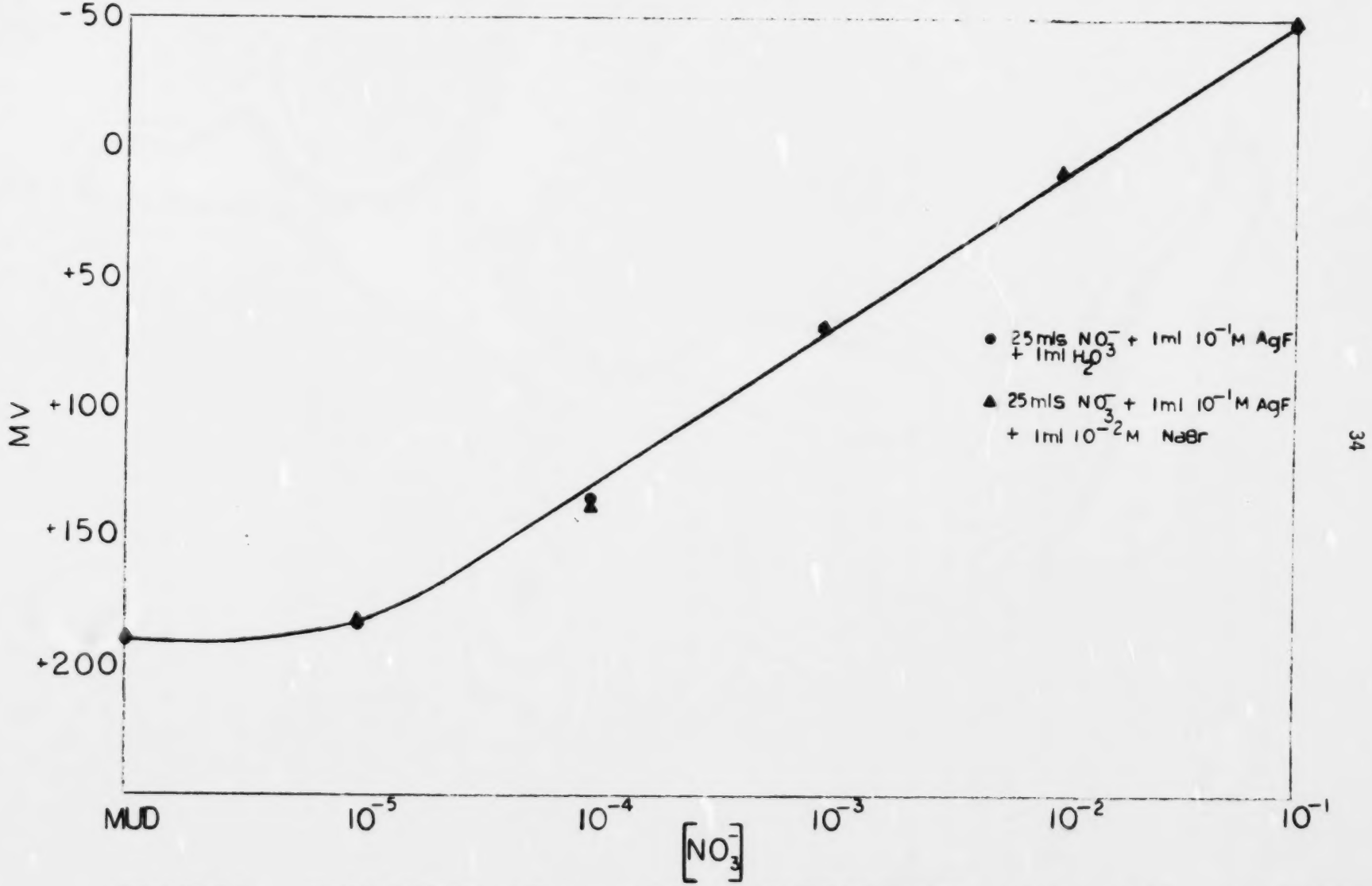

FIGURE 2 ELIMINATION OF HALIDE INTERFERENCE WITH NO_3^- ELECTRODE

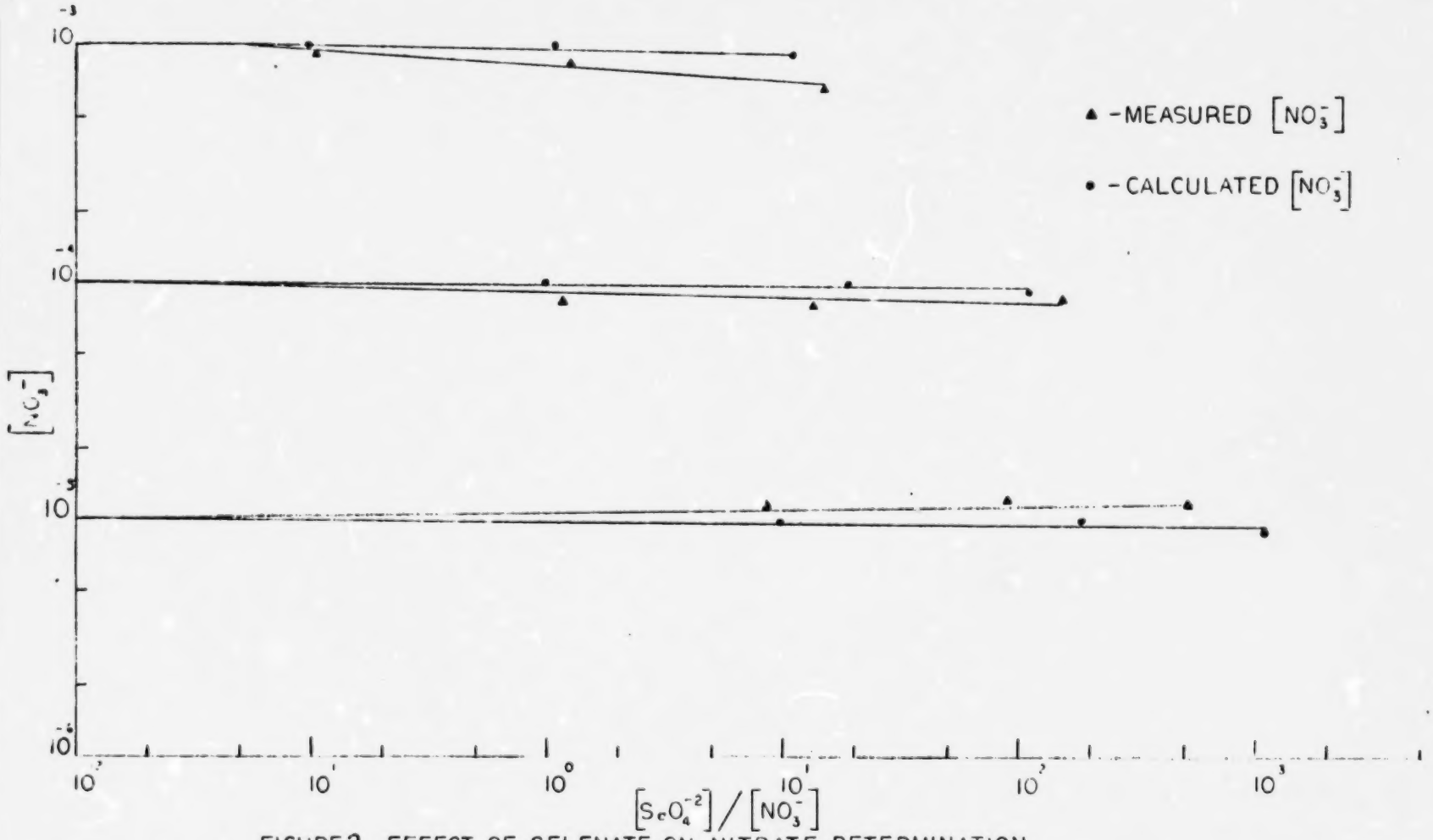

FIGURE 3 EFFECT OF SELENATE ON NITRATE DETERMINATION

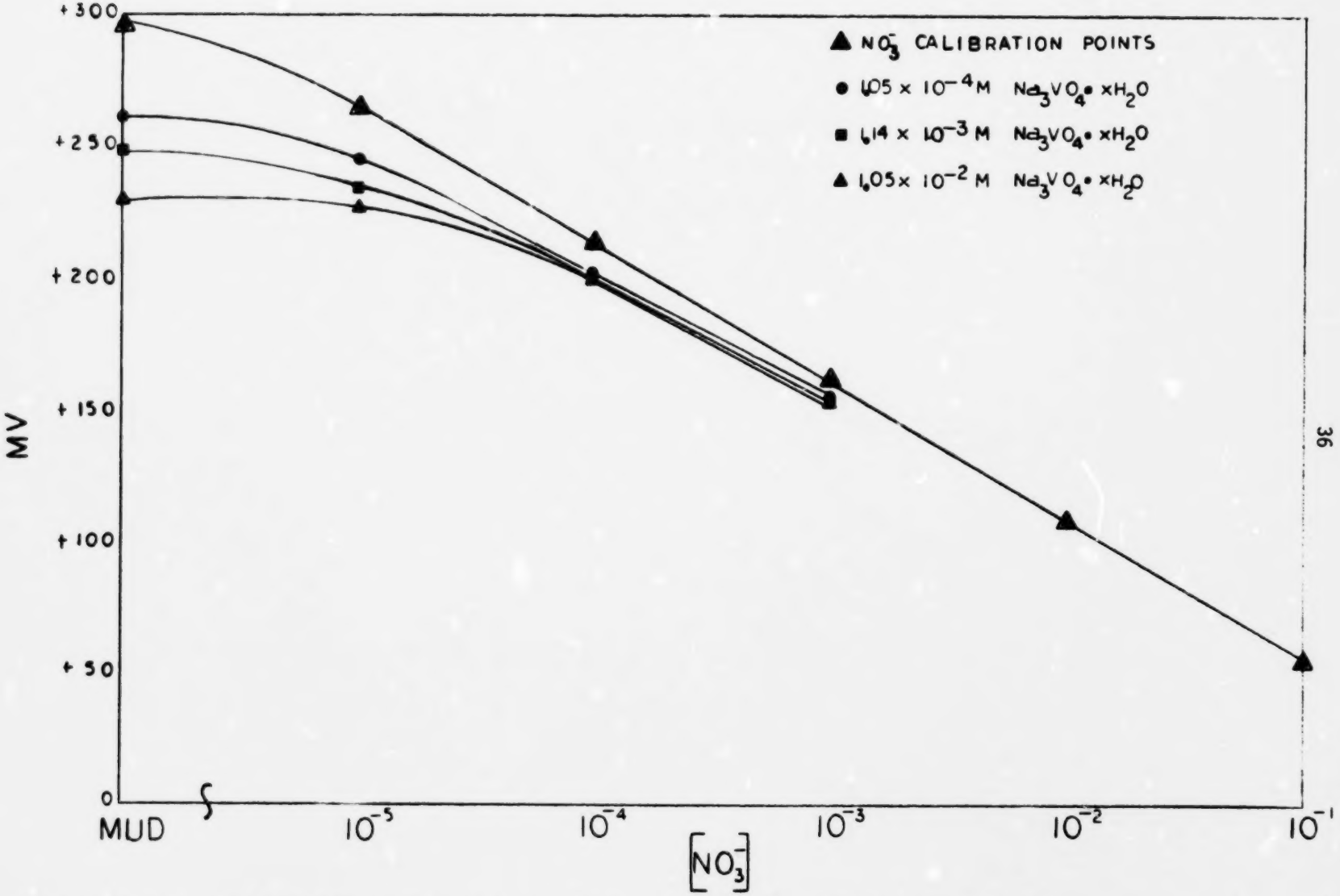

FIGURE 4 EFFECT OF VANADATE ON $[NO_3^-]$ DETERMINATIONS

the interference due to selenium would be minimal. Work with the addition of selenate in the presence of silver fluoride proved that any potential interference due to selenate is removed by the silver fluoride except when the ratio of selenate to nitrate is of the order of 38:1 or greater (Figure 5). Taking into account the large concentration of selenate needed to interfere minimally with the determination of the nitrate concentration ($[SeO_4^{-2}] \geq 38 \times [NO_3^-]$), it is reasonable to consider any selenate interference to be removed by the addition of silver fluoride.

Vanadium also might be an interference with the nitrate electrode. Thus, it was decided that the vanadate interference with the nitrate electrode in the nitrate-fluoride electrode system with silver fluoride present should be investigated. It was found that any potential interference due to vanadate was eliminated by the presence of silver fluoride except when the ratio of vanadate nitrate was equal to or greater than 3.8:1. Since the highest reported ratio of vanadate to nitrate is 1:3 (NASN Air Quality Data, 1966), the presence of silver fluoride in nitrate standards and samples should eliminate the vanadate interference (Figure 6).

This removal of interference is due to the insolubility of silver vanadate and silver selenate.

C. STABILITY STUDY OF THE NITRATE ELECTRODE

The stability study of the nitrate electrode was performed over a period of two months. The data are given in Table XIV.

These data can be used to estimate the probable precision of the method, and to set tentative standardization requirements.

D. NITRATE PROCEDURE DEVELOPMENT

A tentative procedure was developed for the nitrate measurement. This procedure included addition of AgF and used the fluoride reference electrode. This procedure was tested on standards, and the precision of the calibration curve method and standard addition calculation method were compared.

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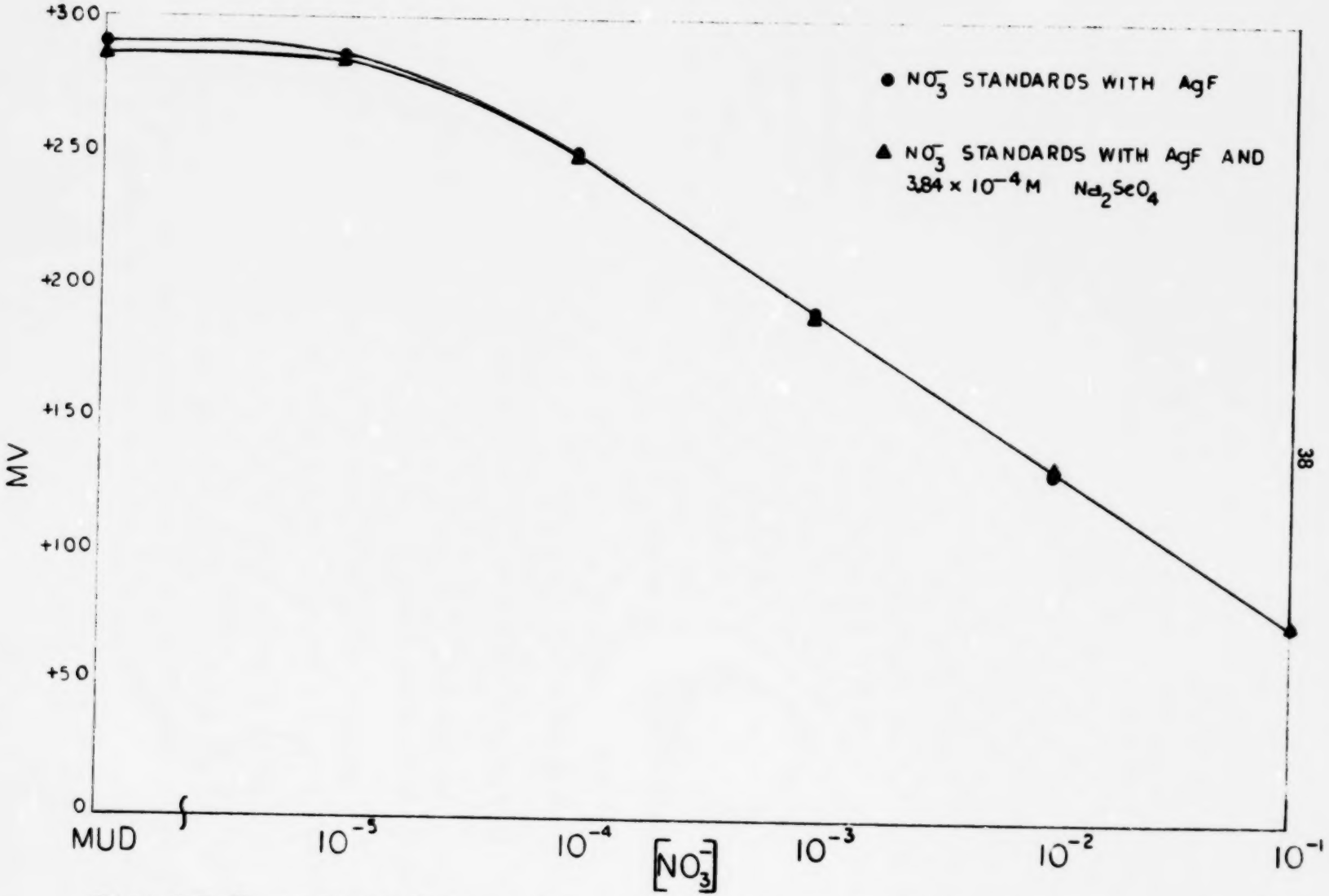

FIGURE 5 ELIMINATION OF SELENATE INTERFERENCE WITH THE NITRATE ELECTRODE

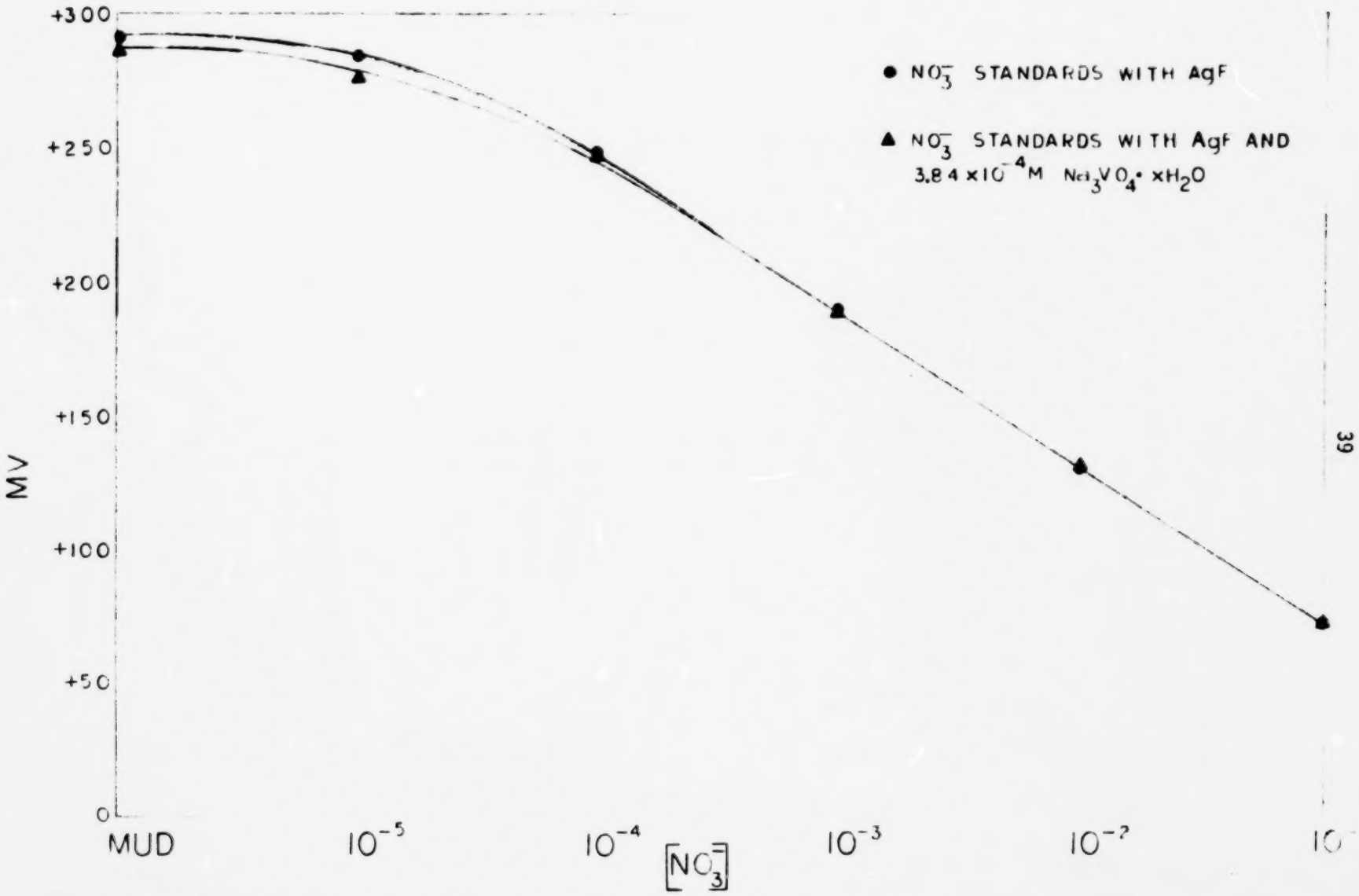

FIGURE 6 ELIMINATION OF VANADATE INTERFERENCE WITH THE NITRATE ELECTRODE

TABLE XIV

STABILITY OF NITRATE ELECTRODE* AS A FUNCTION OF TIME

Date	mv/decade (10^{-2}-10^{-4}M)	mv ($[NO_3^-] = 10^{-2}$M)
9/1/72	54.0	106
9/7/72	53.0	104
9/8/72	55.0	106
9/11/72	53.5	108
9/15/72	56.0	108
9/18/72	53.5	104
9/27/72	56.0	103
9/28/72	51.2	108
9/29/72	56.0	107
10/2/72	55.5	106
10/4/72	56.0	108
10/11/72	54.5	108
10/19/72	51.5	109
10/25/72	56.0	110
Mean	54.4	106.8
Standard Deviation	1.7	2.0

*With fiber tip calomel reference electrode

The method was written as a precursor to the final method which is described in Appendix A. For these tests on nitrate standards, 25 ml of KNO_3 solutions were used.

E. DEMONSTRATION OF THE NITRATE PROCEDURE

1. Calibration Curve Method

For the analysis of this method, nitrate standards with a known amount of silver fluoride added were run in random order (Table XV) in order to determine the accuracy and precision of the electrode method. The results of the statistical analysis of the data obtained on two different days are given in Table XVI. The results obtained on the two different days were then combined despite a possible small difference in the concentration of silver fluoride in the samples. The slopes used to calculate the percentage error were the average of the slopes for the two days. The results of the statistical analysis of the combined data are given in Table XVII.

The percent error was found as follows:

$$E = S \log C + K$$

$$\frac{dE}{dC} = \frac{S}{2.3} \frac{d\ell nC}{dC}$$

$$\frac{dE}{dC} = \left(\frac{S}{2.3}\right)\left(\frac{1}{C}\right)$$

$$(\Delta E) \times \frac{2.303}{S} (100) = \frac{\Delta C}{C} (100)$$

$$(\Delta E) \left(\frac{230.3}{S}\right) = \% \text{ error in terms of concentration}$$

The slope between 10^{-4}M and 10^{-3}M was found by taking the difference in the millivolt readings at these two points. The slopes at 3×10^{-5}M and 10^{-5}M were found by determining the slope of the tangent to these points on the calibration curve.

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TABLE XV

TABLE OF RANDOM NUMBERS

M	No. 1	2	3	4	5
10^{-5}	11	20	5	7	4
3×10^{-5}	16	18	14	12	3
10^{-4}	1	2	21	10	6
3×10^{-4}	25	15	22	17	24
10^{-3}	8	9	23	19	13

TABLE XVI

RANDOM ORDER NITRATE CONCENTRATION DETERMINATIONS

	$[NO_3^-]$	Average (mv)	Standard Deviation (mv) (ΔE)	Slope (S)	% Error*
Day I					
	$10^{-5}M$	+159.66	$\pm$2.61	7.66	62.0**
	$3x10^{-5}M$	+150.32	$\pm$1.71	34.5	11.4
	$10^{-4}M$	+125.66	$\pm$1.65	56.6	6.7
	$3x10^{-4}M$	+ 99.46	$\pm$0.17	56.6	0.7
	$10^{-3}M$	+ 69.02	$\pm$0.33	56.6	1.3
Day II					
	$10^{-5}M$	+163.58	$\pm$1.81	24.0	17.4
	$3x10^{-5}M$	+150.20	$\pm$1.46	45.5	7.4
	$10^{-4}M$	+124.56	$\pm$3.55	57.1	14.3
	$3x10^{-4}M$	+96.66	$\pm$0.89	57.1	3.6
	$10^{-3}M$	+67.42	$\pm$2.78	57.1	11.2

*% error found by $\Delta E \times \frac{230.3}{S}$ = % error

**% error found by graphical method

TABLE XVII

COMBINED RANDOM ORDER NITRATE CONCENTRATION DETERMINATIONS

$[NO_3^-]$	Average (mv)	Standard Deviation (mv)	Slope (S)	% Error
$10^{-5}M$	+161.62	$\pm$2.59	15.8	37.7
$3x10^{-5}M$	+150.26	$\pm$1.81	40.0	10.4
$10^{-4}M$	+125.11	$\pm$2.38	56.9	9.6
$3x10^{-4}M$	+ 98.06	$\pm$1.49	56.9	6.0
$10^{-3}M$	+ 68.22	$\pm$2.21	56.9	9.0

2. Standard Addition Method

In addition to running nitrate concentration determinations in random order on Day II, the standard addition method was also run in random order on the same nitrate samples. A 25 ml aliquot of nitrate standard with AgF was run to determine its initial millivolt reading. The reading was taken two minutes after the electrodes were inserted in the solution, after which time a 1 ml aliquot of a sample 30 or 33 times as concentrated as the original sample was added to the 25 ml aliquot. Two minutes after the addition, the second millivolt reading was taken. From the millivolt change before and after the 1 ml aliquot addition, one is able to obtain the concentration of the initial 25 ml sample as follows:

$$C_{\Delta} = \frac{V_a M}{V_o}$$

where: C_{Δ} is the change in concentration on addition to the sample
V_a is the volume added
M is the molarity of solution added, and
V_o is the original volume of solution

To find the total original concentration, C_o, the equation:

$$C_o = C_{\Delta} \frac{1}{(\text{antilog } \Delta E/S) - 1}$$

was used, with

ΔE = the millivolt change on addition of the known concentration to the original sample, and

S = the slope of the calibration curve at the C_{Δ} point.

The results of the statistical analysis of the data obtained are presented in Table XVIII. Comparison of these data with that of Table XVI, Day II, indicates no advantage to the standard addition method.

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TABLE XVIII

STANDARD ADDITION IN RANDOM ORDER

Initial $[NO_3^-]$	C_Δ	Δ_E	S	$C_{o\,Calculated}$
10^{-5}M	1.2×10^{-5}M	10.2	24	7×10^{-6}M
		10.8		6×10^{-6}M
		12.1		5×10^{-6}M
		10.3		7×10^{-6}M
		9.1		8×10^{-6}M
	Means	$\mu_{\Delta E}$=10.5 mv		μ_{C_o} =6.6×10^{-6}M
	Std. Dev.	$\sigma_{\Delta E}$=1.1 mv		σ_{C_o} =1.1×10^{-6}M
3×10^{-5}M	4×10^{-5}M	16.4	45.5	3.09×10^{-5}M
		16.7		3.01×10^{-5}M
		16.5		3.07×10^{-5}M
		17.4		2.8×10^{-5}M
		15.6		3.33×10^{-5}M
		$\mu_{\Delta E}$=16.5 mv		μ_{C_o} =3.1×10^{-5}M
		$\sigma_{\Delta E}$=0.7 mv		σ_{C_o} =1.8×10^{-5}M

TABLE XVIII (continued)

Initial $[NO_3^-]$	C_Δ	ΔE	S	$C_{o\,Calculated}$
10^{-4}M	1.2×10^{-4}M	17.9	57.14	1.14×10^{-4}M
		17.9		1.14×10^{-4}M
		17.8		1.14×10^{-4}M
		18.3		1.10×10^{-4}M
		18.2		1.11×10^{-4}M
		$\mu_{\Delta E}$=18.0 mv		μ_{C_o} =1.12×10^{-4}M
		$\sigma_{\Delta E}$=0.22 mv		σ_{C_o} =0.02×10^{-4}M
3×10^{-4}M	4×10^{-4}M	20.0	57.14	3.23×10^{-4}M
		20.0		3.23×10^{-4}M
		19.7		3.30×10^{-4}M
		19.8		3.28×10^{-4}M
		19.6		3.32×10^{-4}M
		$\mu_{\Delta E}$=19.8 mv		μ_{C_o} =3.27×10^{-4}M
		$\sigma_{\Delta E}$=0.2 mv		σ_{C_o} =0.04×10^{-4}M

TABLE XVIII (continued)

Initial $[NO_3^-]$	C_Δ	ΔE	S	$C_{o_{Calculated}}$
10^{-3}M	1.2×10^{-3}M	19.6	57.14	9.98×10^{-4}M
		18.7		1.07×10^{-3}M
		17.7		1.15×10^{-3}M
		18.7		1.07×10^{-3}M
		18.6		1.08×10^{-3}M
		$\mu_{\Delta E}$=18.7 mv		$\mu_{C_{o_{Cal}}}$ =1.07×10^{-3}M
		$\sigma_{\Delta E}$=0.7 mv		$\sigma_{C_{o_{Cal}}}$ =0.06×10^{-3}M

F. COLORIMETRIC REFERENCE METHODS

In early tests, nitrate was measured by the electrode and phenol disulfonic acid (PDS) methods. Unfortunately, a high nitrate blank of the filter and problems with the PDS method vitiated these results. However an attempt was made to correct the PDS values for the NO_2^- levels, by running the Griess-Saltzman reaction on these samples. The amount of NO_2^- averaged 6% of the nitrate level on these six samples.

In later tests we used the Sawicki and Scaringelli (1971) nitrate method. In this method NO_3^- is reduced to NO_2^- by hydrazine and the color reaction uses sulfanilamide and N- (1-naphthyl) ethylenediamine as in the Griess-Saltzman reaction.

G. COMPARISON OF ELECTRODE AND COLORIMETRIC NITRATE METHODS ON HIGH VOLUME FILTER SAMPLES

Filter sections were obtained from EPA, courtesy of Ms. Eva Wittgenstein. Random filters were taken from this packet and were designated as S-1 to S-9. The source and weight of these filter sections is shown in Table XIX. All filters were taken at standard conditions (36-47 cfm for approximately 24 hours). Portions of these filters had been previously analyzed by EPA.

These nine sections (48 cm^2) of high volume filters were analyzed for nitrate by the electrode calibration curve method, and by the wet chemical referee method (Sawicki) for nitrate.

The filtrate was diluted from the required 10 ml to 25 ml to allow both the electrode and colorimetric method to be run on the same filtrate. This eliminated variables in the filter sections and leaching. However it caused both methods to be performed on extracts with half the normal nitrate concentration.

The results of this study are shown in Table XX. The test was initially done using only the electrode and Sawicki methods. A portion of this extract was also used for the sulfate analysis (see later

TABLE XIX

SOURCE OF FILTERS FOR COMPARISON DETERMINATION

Walden No.	EPA No.	Site	Particle Wt (g) Total Filter (406 cm^2)
Series 1			
S-1	063384	Bronx, N.Y.	0.252
S-2	065669	Anaheim, Cal.	0.142
S-3	064918	Fairlawn, N.J.	0.041
S-4	064919	Fairlawn, N.J.	0.043
S-5	065888	Elizabeth, N.J.	0.135
S-6	065228	Riverhead, N.Y.	0.142
S-7	065972	Birmingham, Ala.	0.297
S-8	065478	Chattanooga, Tenn.	0.049
S-9	065956	Birmingham, Ala.	0.225
Series 2			
S-11	066000	Birmingham, Ala.	0.216
S-12	065907	Birmingham, Ala.	0.034
S-13	065889	Elizabeth, N.J.	0.090
S-14	064899	Ridgewood, N.J.	0.103
S-15	065672	Anaheim, Cal.	0.163
S-16	064917	Fairlawn, N.J.	0.071
S-17	063385	Bronx, N.Y.	0.218
S-18	065689	Santa Monica, Cal.	0.067
S-19	065310	Magna, Utah	0.126
S-20	064248	Charlotte, N.C.	0.121

TABLE XX

INITIAL NITRATE ANALYSIS

Sample No.	Nitrate in Filter Extract (µg/48 cm^2) Electrode 1	Electrode 2	Sawicki 1	Sawicki 2	PDS (2)
S-1	486	310	313	195	170
S-2	3180	2320	1880*	1270*	1880*
S-3	230	149	150	116	16
S-4	197	67	59	58	20
S-5	736	496	433	337	307
S-6	408	102	144	69	80
S-7	962	666	603	485	134
S-8	226	194	81	57	11
S-9	470	248	279	220	157
Blank		34		25	29
Blank		33		25	

* Outside range of colorimetric procedure

section). The test was repeated using a separate section of the filter, and using the electrode, Sawicki, and phenol disulfonic acid (PDS) procedures. Sample S-2 was not measured accurately by the Sawicki method and perhaps not by PDS. Also it was too highly weighted in correlation coefficients. Calculated correlations, without S-2, are given in Table XXI.

The correlation between the three methods was not as good as anticipated, presumably because of laboratory inaccuracy. Correlation within each method on two sections of the same filter also showed large variability. In these tests the electrode method gave a 30-40% higher value, which would also be a problem of the method.

Therefore the test was repeated, adding a known quantity of nitrate to each sample. The initial quantity and the incremental increase were analyzed by the electrode, Sawicki and PDS methods. For this study new filters had to be used. These are described as S-11 through S-20 in Table XXII. The equivalent of two strips ($97cm^2$) were leached in 50 ml of water.

The results of these tests are described in Tables XXIII through XXV and Figures 7 through 9 . In these tests there is an excellent one-to-one correlation between the methods. One sample (S-11) appears to have an unusually high nitrate value according to the electrode method. This is one of two samples from Birmingham, Alabama. We have no explanation for this difference. However, since the value is outside of 2.5 standard deviation the values are recalculated without this entry. The standard deviations between the methods are shown in Table XXIV. There is a ±46 mg (NO_3^-) error between the electrode and the Sawicki methods (including the 207 mg error on the 2903 mg S-15 value). Similarly, there is a 13% relative standard deviation (including the 9 mg error on the 24 mg S-20 sample).

Recoveries of nitrate by the three methods are also satisfactory (Table XXV). The low value of the Sawicki method is presumably due to the lack of reagent for the high nitrate values. Thus we are outside of the range of the method. The large recovery (125%) by the electrode method is unexplained. However, a lower recovery accuracy of the electrode method is due to the 124 mg

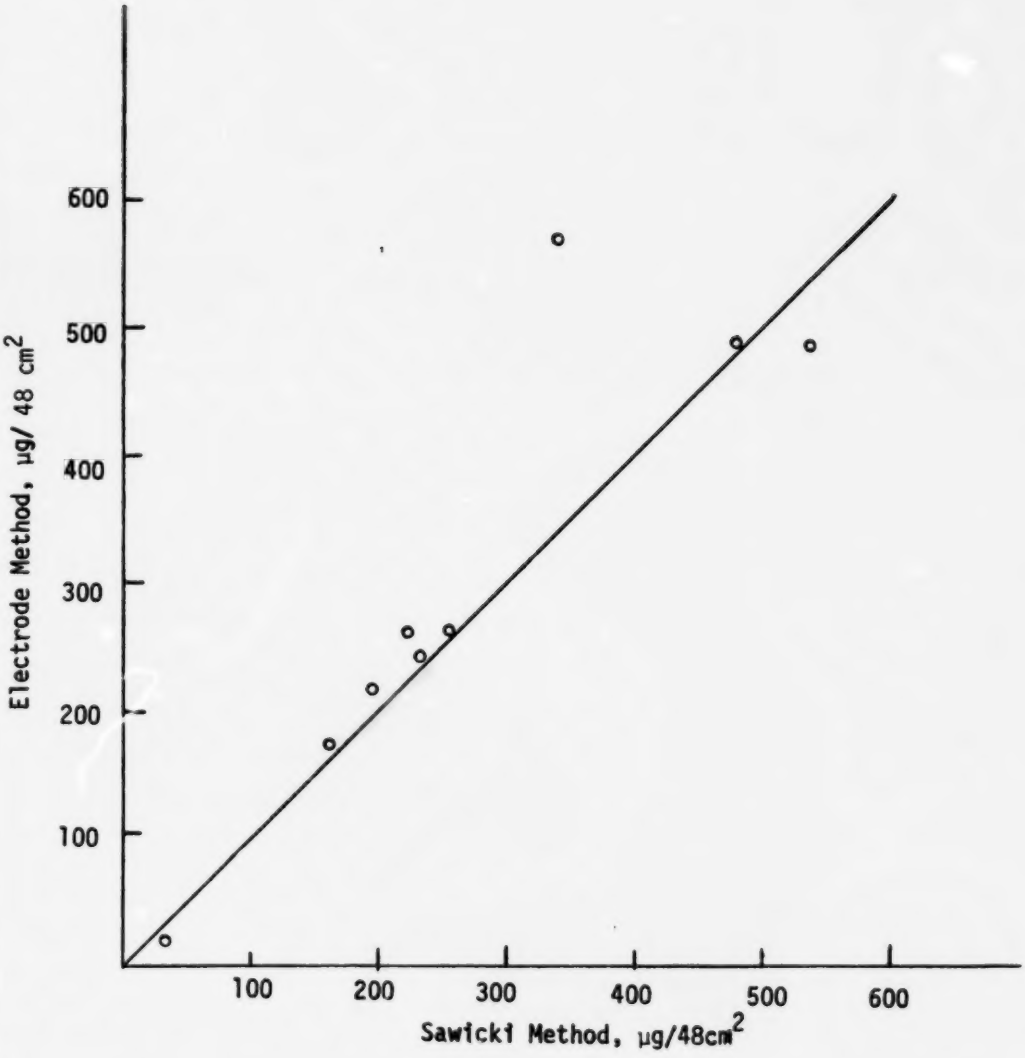

FIGURE 7 . COMPARISON OF ELECTRODE AND SAWICKI METHODS
(Perfect Correlation Line Drawn)

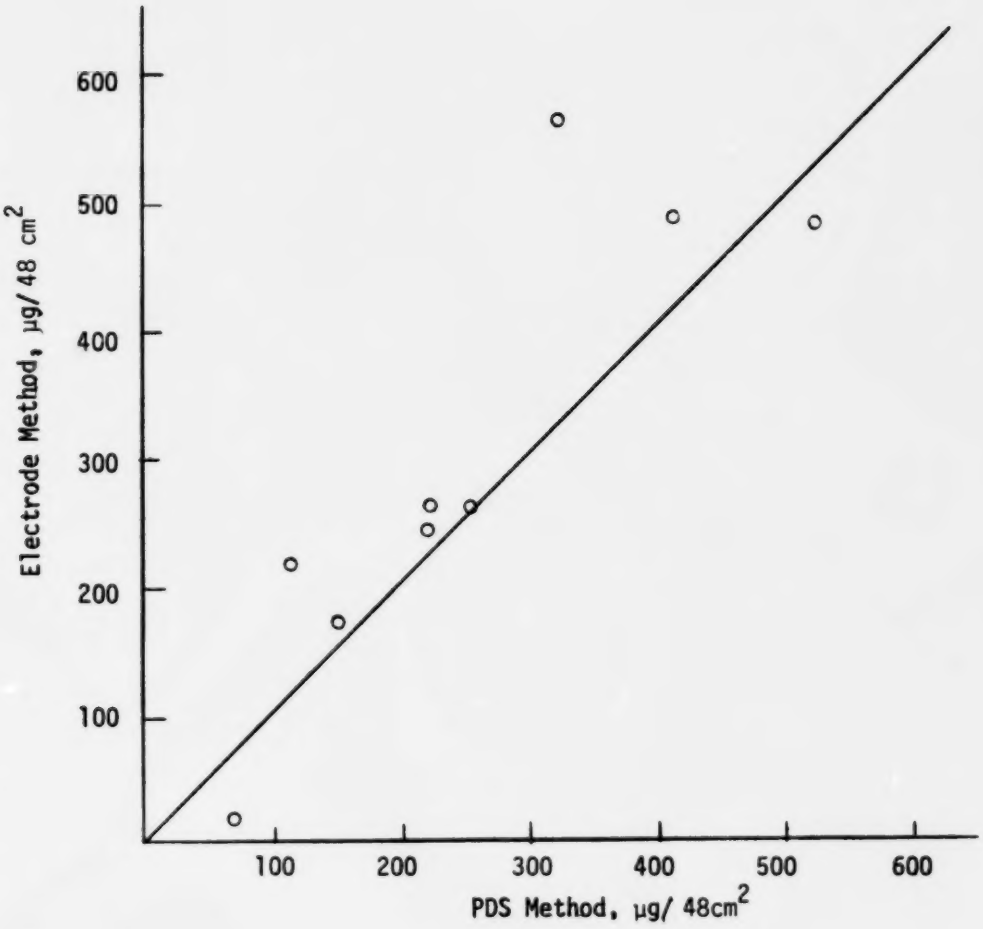

FIGURE 8. COMPARISON OF ELECTRODE AND PDS METHODS

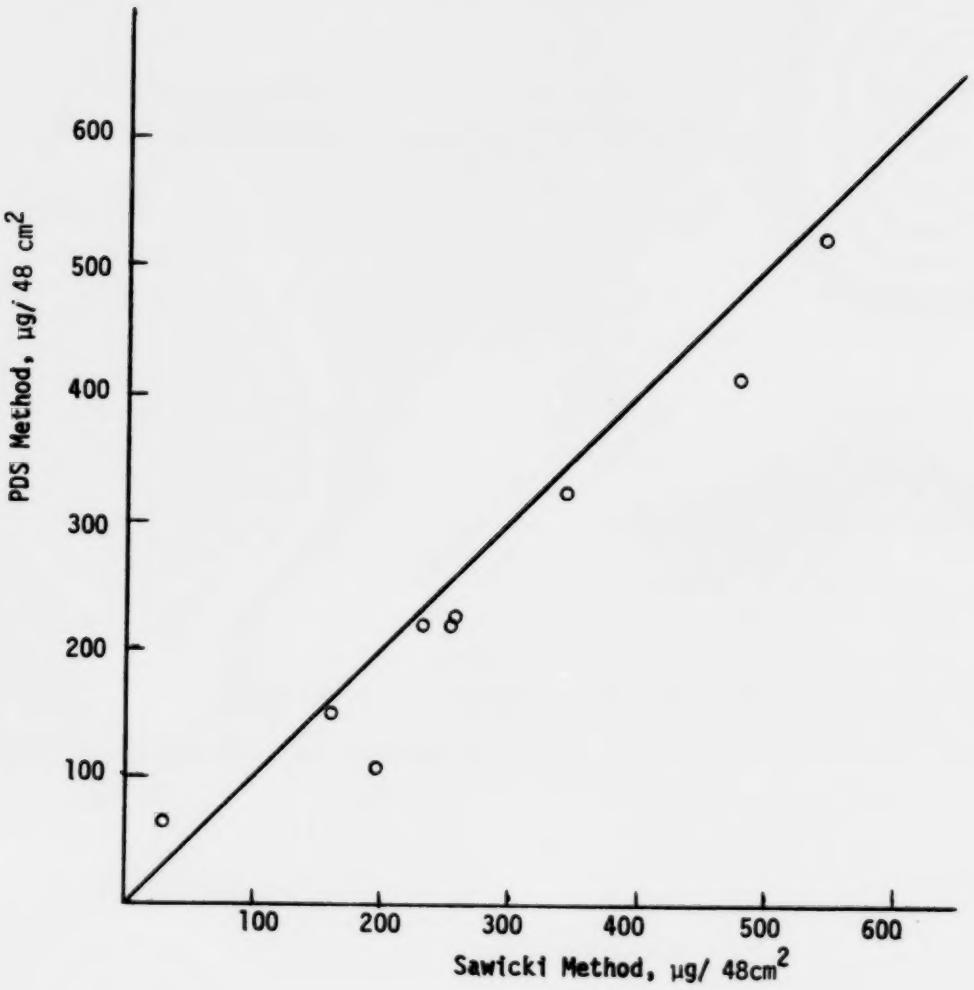

FIGURE 9. COMPARISON OF PDS AND SAWICKI METHODS

TABLE XXI

CORRELATIONS OF INITIAL NITRATE DATA*

Methods	Correlation Coefficient(r)	Linear Regression (y = electrode, x = colorimetric)
Electrode - Sawicki (1)	0.978	y = 1.40x + 104
Electrode - Sawicki (2)	0.971	y = 1.31x + 28
Electrode - PDS	0.660	y = 1.34x + 129

* S1 - S9 excluding S-2 which is outside of colorimetric range

TABLE XXII

ELECTRODE DATA FOR HI VOL NITRATE MEASUREMENT

Sample	% of Extract (for 48 cm^2)	E vs F^- Reference (mv)	Calc NO_3^- Molarity ($x10^4$)
S-11	100	226	3.65
S-12	100	250	1.40
S-13	100	245	1.70
S-14	100	256	1.12
S-15	100	183	19.4
S-16	100	229	3.15
S-17	100	247	1.58
S-18	80	224	3.90
S-19	100	245	1.70
S-20	100	298	0.13

TABLE XXIII

REPEAT OF NITRATE ANALYSIS OF HI VOL SAMPLES

	Nitrate in Filter Extract ($\mu g/48\ cm^2$)		
Sample	Electrode	Sawicki	PDS
11	566	342	324
12	217	194	114
13	264	256	224
14	174	160	150
15	3007	2800	2824
16	488	477	414
17	245	232	220
18	484	543	524
19	264	221	254
20	20	29	68

TABLE XXIV

CORRELATIONS OF NITRATE ANALYSIS

Methods	Correlation* Coefficient	Linear Regression* (Y=electrode, x=colorimetric)
Electrode-Sawicki	0.896	$y = 0.989x + 33$
Electrode-PDS	0.869	$y = 1.05x + 36$
Sawicki-PDS	0.971	$y = 1.06x + 3$
Electrode-Sawicki**	0.986	$y = 0.911x + 29$
Electrode-PDS**	0.945	$y = 0.954x + 35$

Std. Dev. $\simeq$ Ave. Dev. x $\frac{2}{\sqrt{\pi}}$

Assumes: Electrode (y) = Colorimetric (x)

	mg	%
Electrode-Sawicki	69	17
Electrode-PDS	89	34
Electrode-Sawicki**	46	13
Electrode-PDS**	69	31

* Analysis without S-15

** Analysis without S-11, which is outside 3 Std. Dev.

TABLE XXV

RECOVERY OF NITRATE ADDED TO HI VOL SAMPLES

Sample	Recovery of 124 µg[1] Electrode	Sawicki[4]	PDS[4]
S-11	(154[3])	108	128
S-12	160	107	127
S-13	155	104	130
S-14	135	97	127
S-15	(374[3])	(21[4])	120
S-16	190	80	129
S-17	164	86	129
S-18	(295[3])	(55[4])	124
S-19	145	95	123
S-20	139	100	122
Average	155.4	97.1	125.9
Std. Dev.	18.6	9.3	3.4
% Recovery ± Std. Dev.	125±12	78±10	101±3

(1) Data in parentheses not used in calculation.

(2) Only 1/5 of extract used (5 ml). Hence these recoveries are 5 times larger relative to the sample concentration.

(3) Increment too small to measure accurately (< 25% initial value).

(4) Value outside range of method.

of nitrate being added to five times the amount of sample used for the colorimetric analyses.

VI. SULFATE ELECTRODE METHOD

A. SULFATE ELECTRODE APPROACHES

Early in the program a sulfate electrode was prepared by Orion Research Inc. according to Rechnitz et. al. (1972). This electrode was reported by Rechnitz to have a Nernstian response for $SO_4^{=}$ down to 10^{-4} molar. We found ∿25 mv/decade between 10^{-1} and 10^{-2}M and ∿5-10 mv/decade below 10^{-2}M. Although a reading is obtained, it is not clear that the electrode is actually responding to sulfate. This approach did not appear very promising since the electrode had to be soaked prior to analysis, the response time was slow, and the sensitivity inadequate.

A later article by Rechnitz and Mohan (1973) prompted us to contact Prof. Rechnitz to ask if we could borrow an electrode for testing on this program, and also whether or not there were cation interferences (e.g. Pb^{++}). Prof. Rechnitz replied that he had received numerous requests for electrodes since 1972, and was unable to meet these requests. Thus they published the second paper giving complete instructions for making the electrode. He also mentioned that cation interferences had not been determined.

We did not pursue this approach any further.

It should also be mentioned that sulfate electrodes have been prepared by other investigators, using an insoluble precipitate in a polymer matrix. Saunders has developed such a system ($BaSO_4$) and this is published as U. S. Patent No. 3,709,811 (Government-owned invention).

Jasinski and Trachtenberg also have a government-owned application (No. 350-444) which describes a determination of sulfate using a ferric ion-selective electrode.

The method which we pursued was the titration of the sulfate with $Pb(ClO_4)_2$ and measurement of the excess lead with an Orion lead electrode. This concept is described by Orion (1972), and by Ross and Frant (1969).

B. SOLUBLE SULFATE INTERFERENCES

In the determination of sulfate by the precipitation with lead, two types

of interferences are possible. These are:

(1) Metals which respond at the lead electrode.
(2) Other anions which precipitate with lead.

However, only those materials which would be soluble in air pollution samples need be considered. Fortunately, materials which precipitate with sulfate, such as lead, are not potential interferences since the precipitate will form and these metallic sulfates are not expected to be found in the leached sample. If we were attempting to measure total sulfate, these would be interferences.

However, potential anion interferences should be considered in view of possible lead precipitates with the titrant. If a significant concentration, relative to sulfate, exists in the solution, then titration of these anions with $Pb(ClO_4)_2$ will cause a positive error in the sulfate determination. Lead halides, fortunately, are relatively soluble, and lead vanadate is slightly soluble. However, the error from other anions (e.g. $Sb_2O_7^{-4}$, AsO_4^{-3}, HBO_3^{-2}, $H_2PO_3^{-}$, SeO_4^{-2}, CrO_4^{-2}, MoO_4^{-2}, MnO_4^{-2}) which form lead precipitates should be considered further. We believe that these anions will be found in lower concentrations than the endogenous lead in most instances. Thus, these may exist only as insoluble precipitates. However, there is more sulfate than lead, hence, much of the lead is tied up in the sulfate precipitate. The quantity of interfering anions that are soluble is probably best determined experimentally. Thermodynamically anions which form more insoluble lead salts than $PbSO_4$ should precipitate in preference to $PbSO_4$ during the leaching process, and lead salts that are more soluble than $PbSO_4$ should not interfere.

The only practical test of this form of interference is by the correlation of electrode and chemical measurements of exposed filters.

The lead electrode is relatively insensitive to other metals. Appreciable quantities of copper, mercury, and silver poison the electrode, and iron and cadmium interfere at concentrations above the concentration of lead. Most of these materials form insoluble sulfates and will therefore not be found in the leached sample.

The remaining ions (especially Cu^{++}) could be complexed with citrate or ammine complexers, if necessary.

C. PRELIMINARY SULFATE STUDIES

1. Solvent Studies

A problem appeared when low levels of sulfate ($< 5 \times 10^{-4}$M) were analyzed due to the solubility of $PbSO_4$ in aqueous solution ($K_{sp} = 1.6 \times 10^{-8}$). Therefore, a study of different solvents was undertaken so the K_{sp} could be sufficiently lowered to determine low levels of sulfate. The concentrations of the solvents were varied and the time to reach equilibrium was noted.

The lead electrode was set up with the double junction reference electrode. The reference electrode had 1M $NaNO_3$ in the outer chamber. To two milliliters of 10^{-3}M lead, water and solvent were added to bring the sample volume to 18 ml. The reference potential was recorded (10^{-4}M Pb^{++}) and 2 ml of 10^{-3}M SO_4^{-2} were added. When the potential reading stabilized, the time and potential were recorded again ($Pb^{++} = \sqrt{K_{sp}}$).

The data of Table XXVI summarize this study. The equilibration time is the minutes required to come within 2 mv of the final reading. The Δ mv value is the difference, between the solvent system and water, for the change occurring after the addition of sulfate. Thus,

$$\Delta \text{ mv} = (E_{Pb = \sqrt{K_{sp}}} - E_{Pb = 10^{-4}})_{solv} - (E_{Pb = \sqrt{K_{sp}}} - E_{Pb = 10^{-4}})_{H_2O}.$$

Based on this study, which is summarized by Figure 10, a series of calibration curves (known subtraction study) were prepared using solutions of 50% methyl cellosolve acetate in water and 50% methanol in water. The methanol calibration is included to show the increased sensitivity obtained by using the cellosolve acetate which lowers the K_{sp} of $PbSO_4$ by at least one order of magnitude over that of methanol at the 50% solvent concentration. This K_{sp} is at least two orders of magnitude lower than aqueous solution, or less than 10^{-10}. Sulfate in the range of 10 to 500 µg may therefore be determinable.

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TABLE XXVI

EFFECT OF SOLVENT ON THE K_{Sp} OF $PbSO_4$

Methanol %	0	10	20	30	40	50	60	70	80
Equilibration Time	*	3	12	7	4	3	2	1	3
Δ mv	-	4	6	13	22	38	58	74	89
Acetone %	0	10	20	30	40	50**	60**	70**	80**
Equilibration Time	2	1	4	5	2	4	5	2	3
Δ mv	-	2	9	23	28	42	69	91	128
Dioxane %	0	10	20	30	40	50	60**	70**	80**
Equilibration Time	10	6	14	7	3	3	3	9	7
Δ mv	-	-21	-8	4	12	31	58	63	81
Methyl Cellosolve %	0	10	20	30	40	50	60	70	80**
Equilibration Time	7	*	2	3	4	4	3	2	2
Δ mv	-	-1	-8	-1	13	30	49	72	106
Methyl Cellosolve Acetate %	0	10	20	30	40	50	60	70**	80**
Equilibration Time	10	9	10	2	1	3	2	2	2
Δ mv	-	14	27	36	40	57	76	96	122

*No change of reading (< 2 mv)

**No precipitate evident

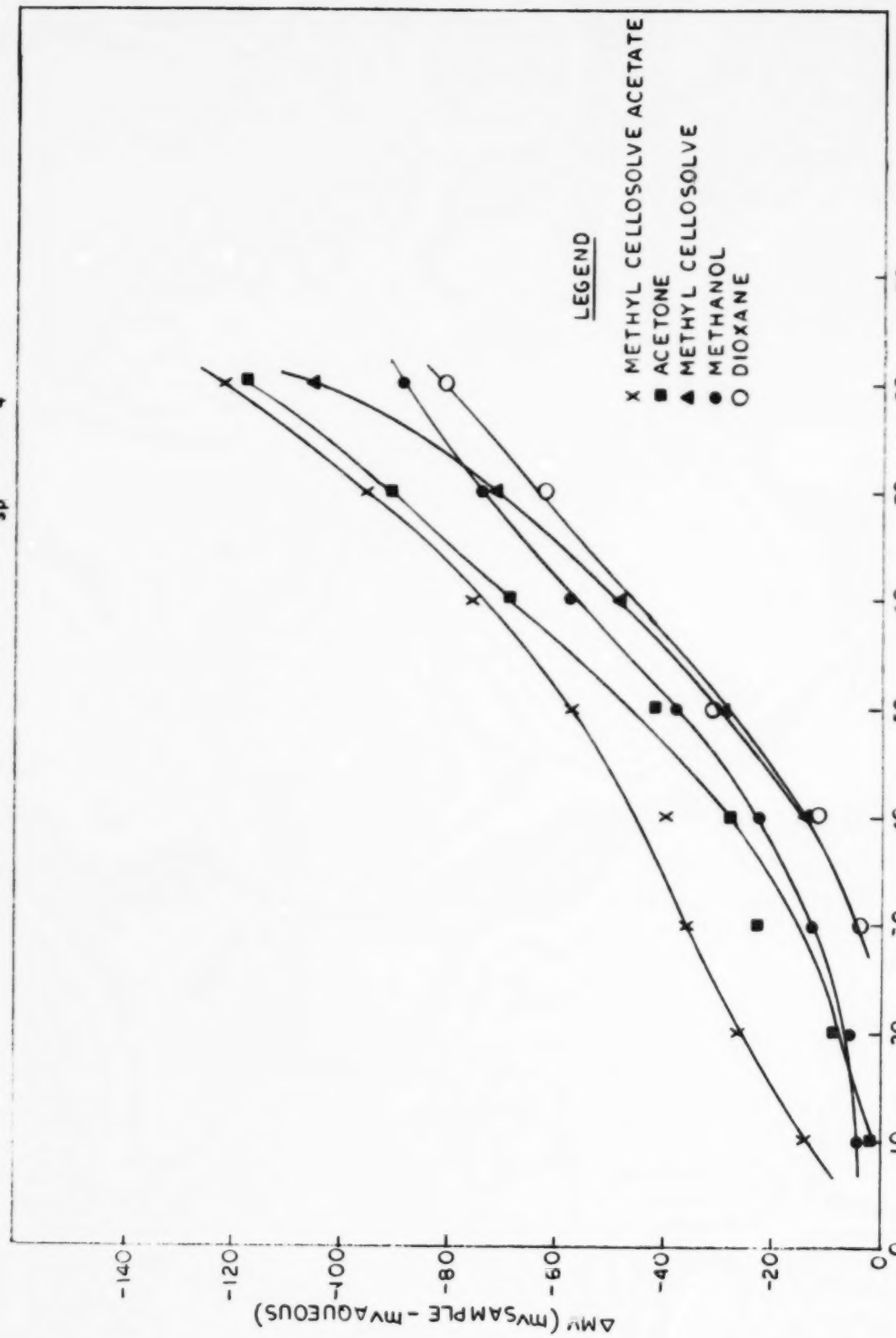

Figure 10. Solvent Effect on the K_{sp} of $PbSO_4$.

2. Known Subtraction Study

The major effort was placed on developing the method of known subtraction as a means of determining sulfate. This involves the addition of sulfate to a known amount of lead and monitoring the change in potential with an ion-selective lead electrode. The quantity of lead must be greater than the quantity of sulfate. The decrease in lead concentration after addition of sulfate gives the measurement of sulfate.

Initially, varying amounts of standard aqueous sulfate were added to a standard lead solution in 50% methanol. The results were inaccurate since various dilution factors were introduced and the solvent (methanol) was not kept at a constant 50%. It was also found that about 8 minutes were required between additions, in order to reach equilibrium.

In later experiments the sulfate solution was also prepared with 50% solvent. The data of these experiments are plotted in Figures 11-14. The data are plotted linearly, since this approximation is sufficient for a logarithmic response over a small range of concentrations.

Figures 11 and 12 represent the upper calibration range, that is, 48 to 480 µg of SO_4^{-2}. The only difference is the solvent used. As can be seen, the potential change from 3.8×10^{-4}M to 2×10^{-4}M is greater when the methyl cellosolve acetate is used than when methanol is used (16.3 mv versus 10.9 mv). Figures 13 and 14 show the lower range, 4.8 to 48 µg SO_4^{-2}. Again the cellosolve acetate responds with a greater potential change when the lead concentration changes from 7.8×10^{-5}M to 6.0×10^{-5}M. This is 7.2 mv compared to 4.4 mv.

The difference in sensitivity is primarily due to the use of different (not decade different) lead solutions for these tests (i.e., 4×10^{-4}M for high range and 8×10^{-5}M $Pb(ClO_4)_2$ for the low range).

3. Comparison to Titration Method

The known subtraction method is better than the potentiometric titration for the determination of ambient levels of SO_4^{-2}. A minimum of 10 points is required to obtain a titration curve while only one determination is required for known sub-

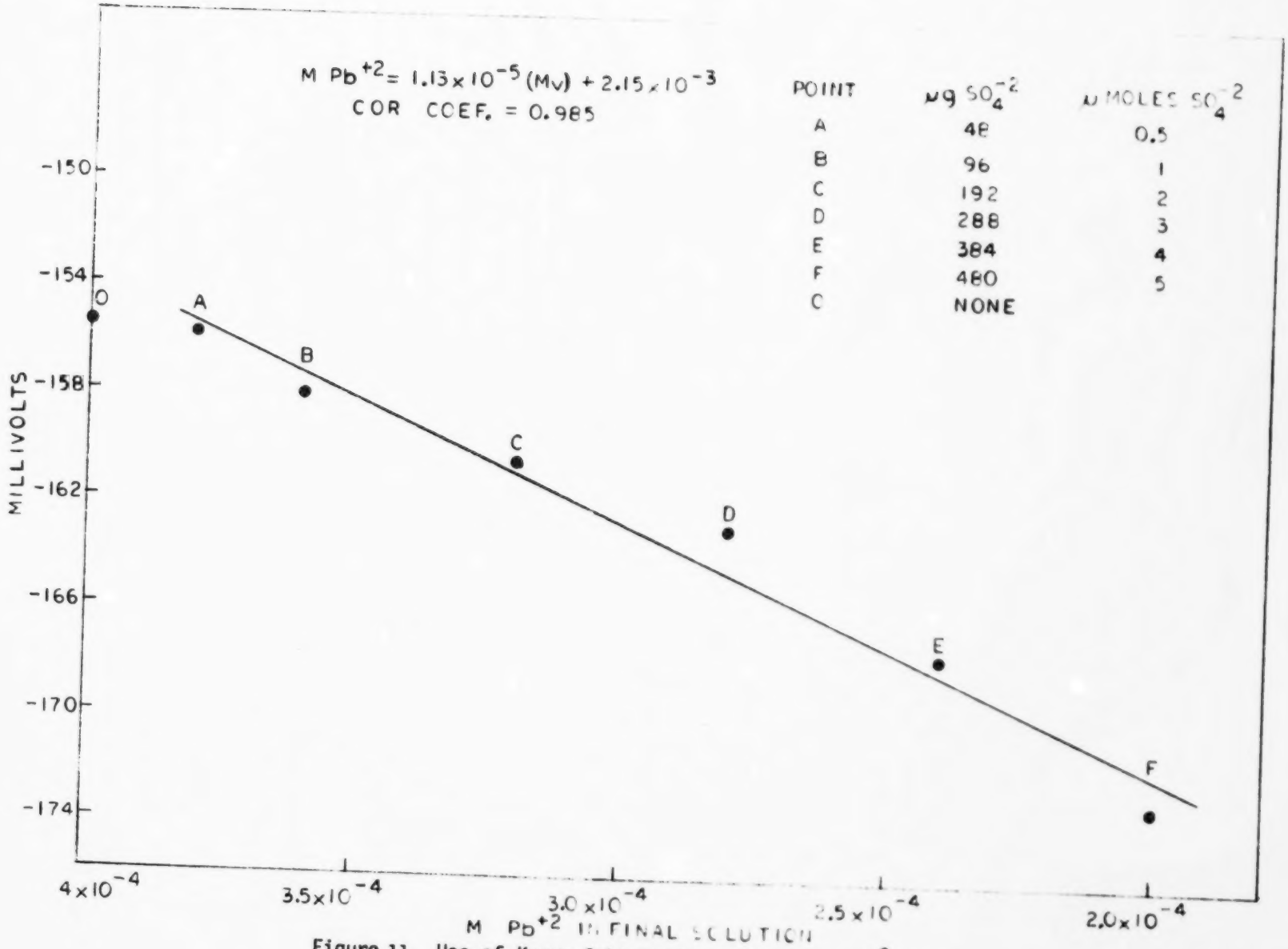

Figure 11. Use of Known Subtraction Method for SO_4^{-2} Detection. Methyl Cellosolve Acetate

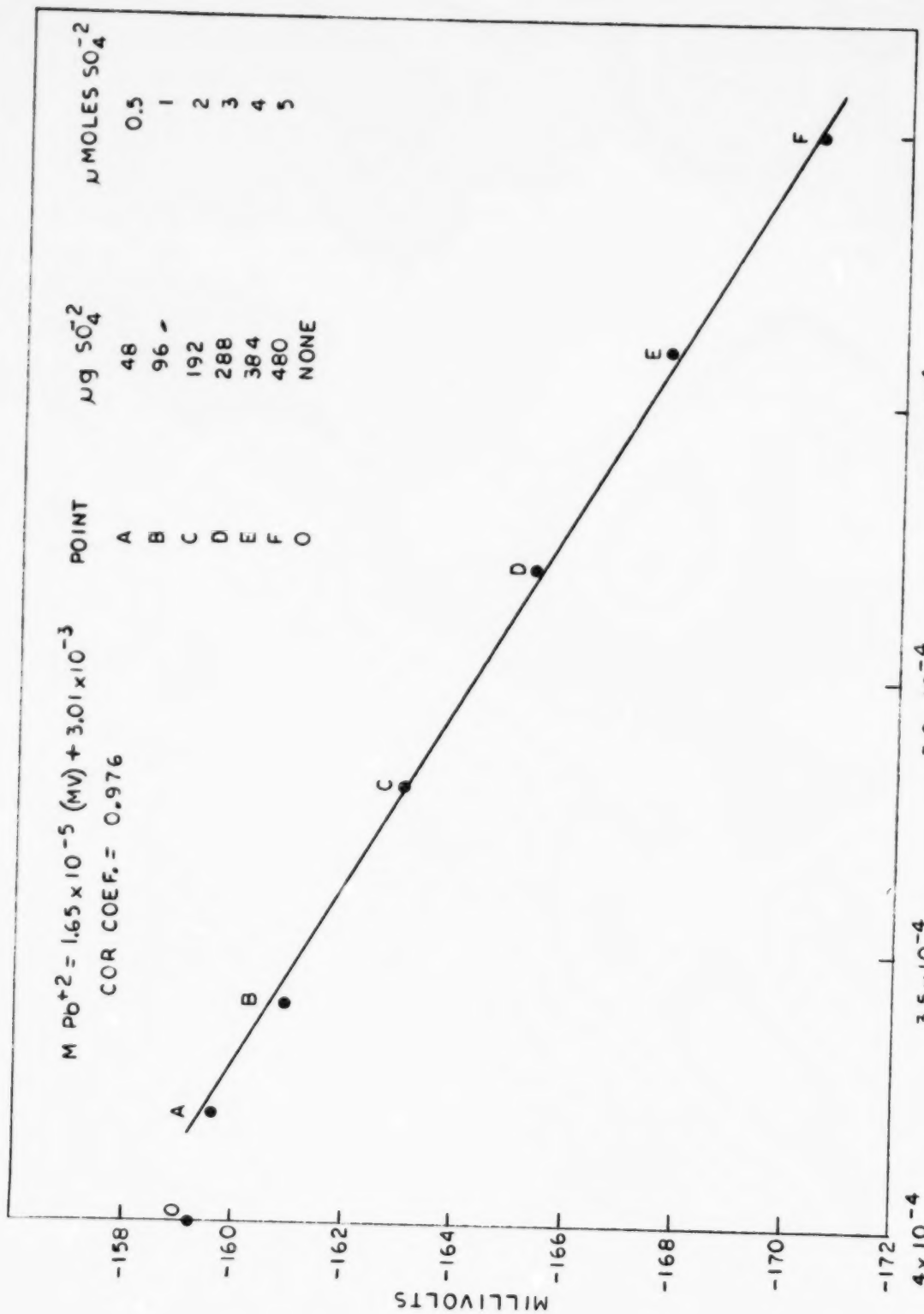

Figure 12. Use of Known Subtraction Method for SO_4^{-2} Detection.
Methanol

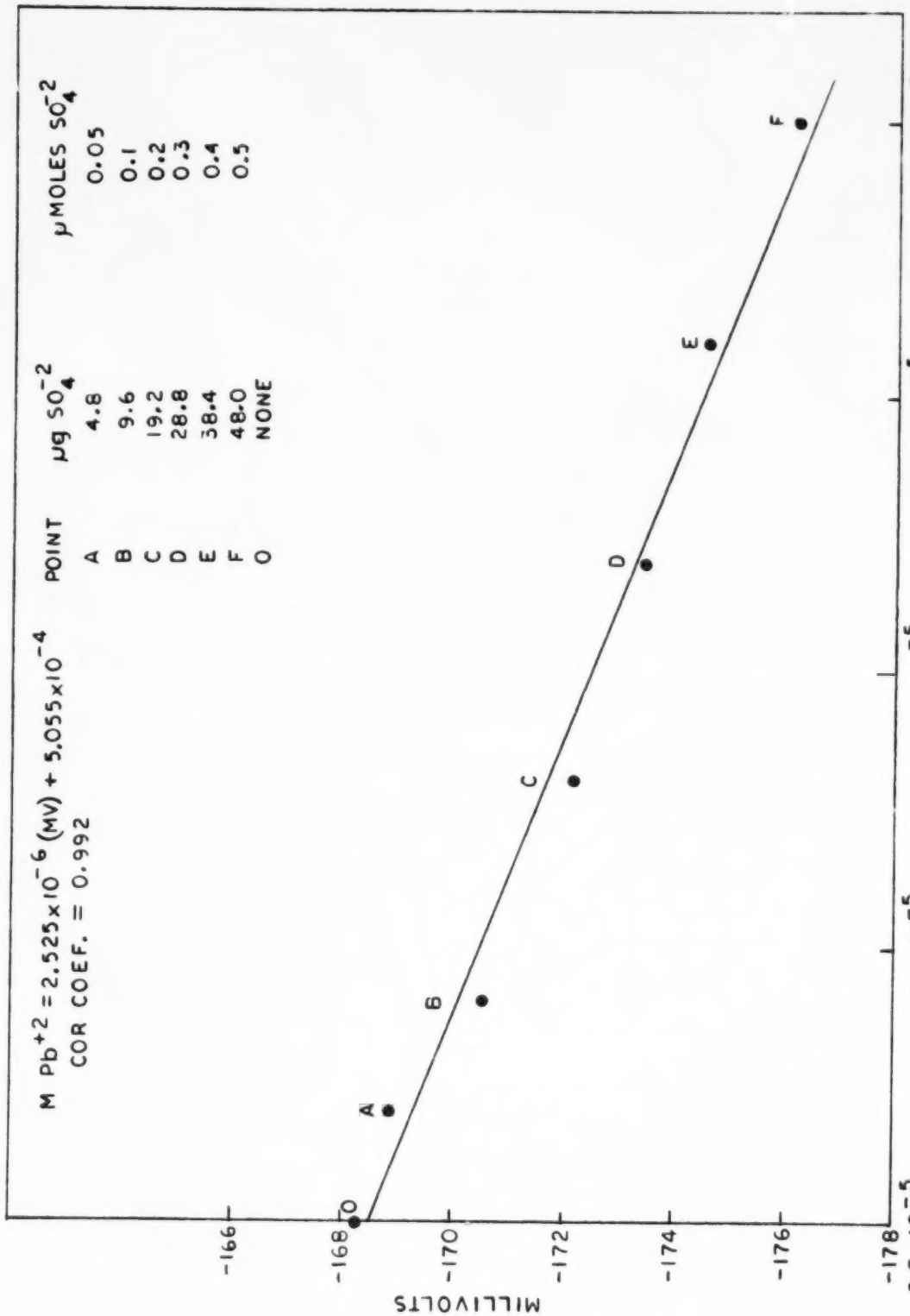

Figure 13. Use of Known Subtraction Method for SO_4^{-2} Detection.
Methyl Cellosolve Acetate

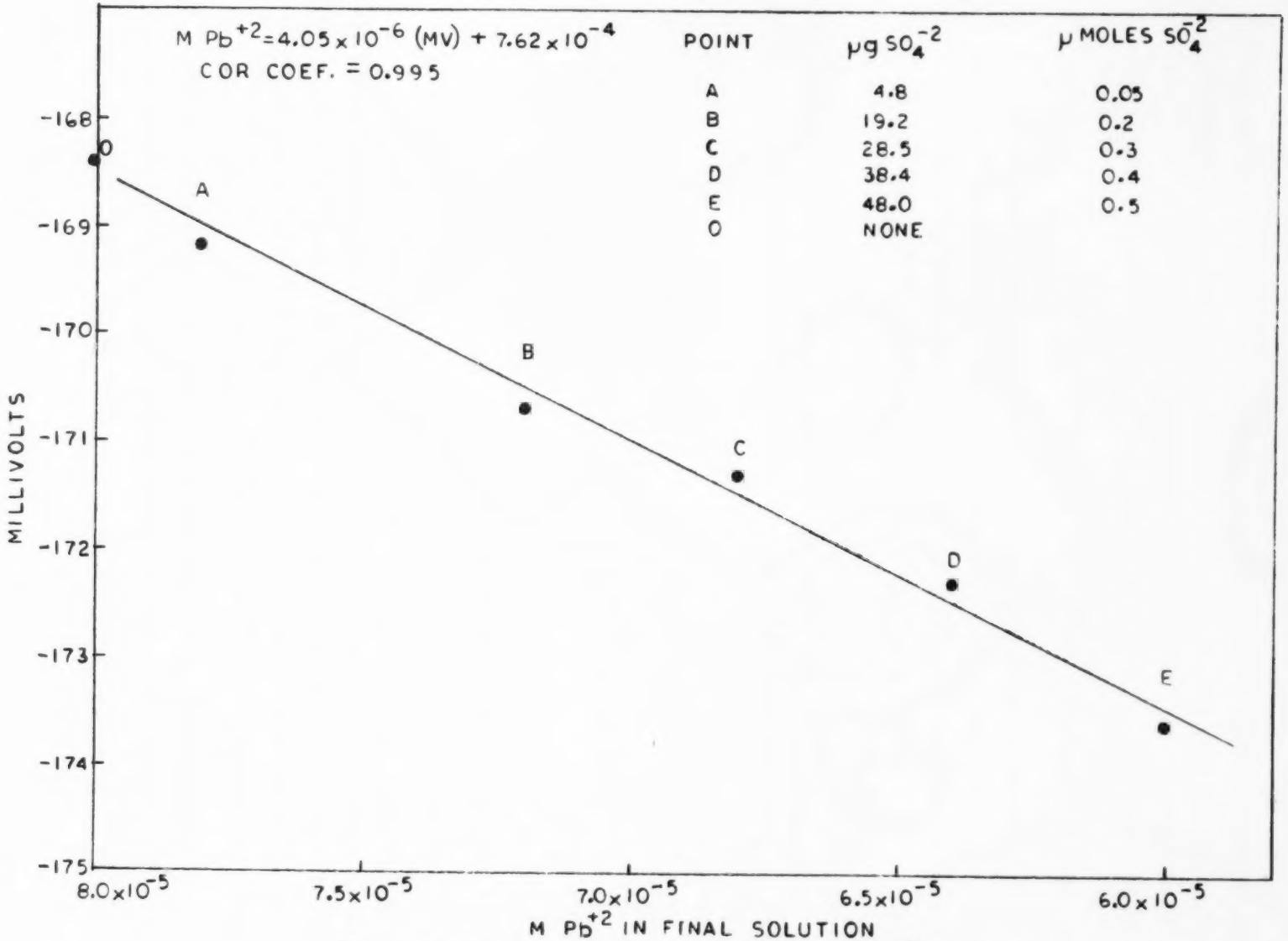

Figure 14. Use of Known Subtraction Method for SO_4^{-2} Detection. Methanol

traction method. Another disadvantage with the titration is a very shallow endpoint break, which requires that the first derivative be taken to accurately describe the endpoint. Figure 15 shows such an example where the sulfate level was found to be 8.3 $\mu g/m^3$ or 3.0 x 10^{-4}M. This experiment was performed in 50% methanol.

D. ANTICIPATED SULFATE ACCURACY BY STANDARD SUBTRACTION

Measurement of sulfate by measuring lead ion decrease requires that the quantity of lead be greater than that of sulfate. However, if the sulfate quantity is much smaller than the lead, then the precision of the method will be poor. In this case, a large change in sulfate will result in only a minor change of the lead concentration.

Calculations were therefore made to determine how many lead solutions would be required to achieve reasonable accuracy in the sulfate determination. The primary equation is:

$$E - E_o = 29 \log ([Pb]_o - [SO_4]) - 29 \log [Pb]_o$$

$$\Delta E = 29 \log \frac{[Pb]_o - [SO_4]}{[Pb]_o}$$

where:

$[Pb]_o$ is the initial quantity of lead, and

$[SO_4]$ is the quantity of sulfate.

We assume no volume change or dilution in this analysis. We will let $[Pb]_o = 1$ and calculate the relative quantities of sulfate to lead with the corresponding millivolt change. Reasonable choices of initial lead concentrations are of the ratio 0.1:1.0:10, 0.1:0.3:1.0:3.0:10, or 0.1:0.2:0.5:1.0:2.0:5.0:10. The calculated response for these increments is shown in Table XXVII and Figure 16.

The concentration error associated with an electrode error can be found by analyzing the slope of the curves of Figure 16. Alternately, this slope can be determined mathematically by differentiating the above equation. Thus,

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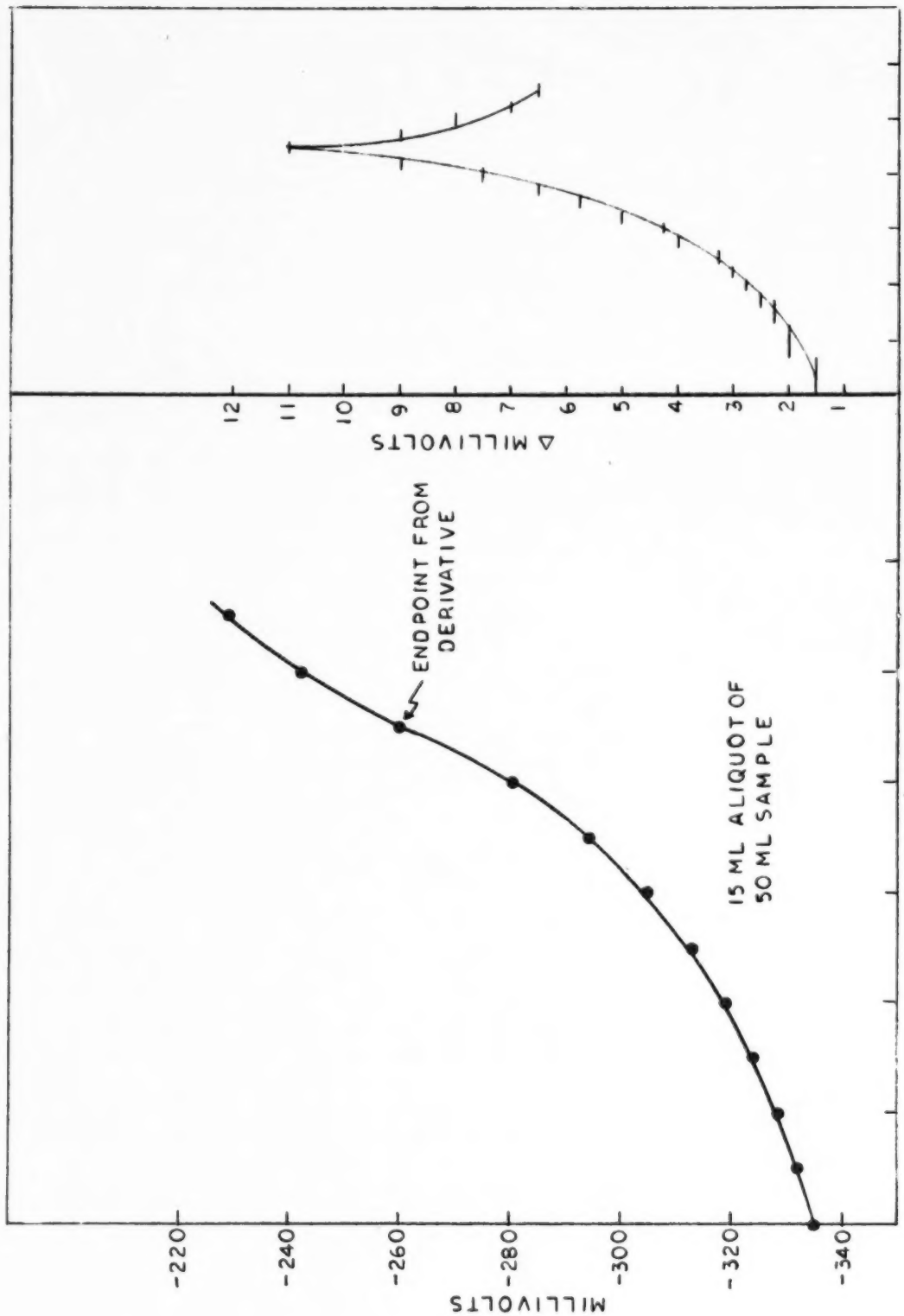

Figure 15. Potentiometric Titration and First Derivative for SO_4^{-2} Detection.

TABLE XXVII

CALCULATION OF ELECTRODE RESPONSE WITH VARIOUS RATIOS OF SO_4/Pb

$(SO_4)/(Pb)$	$(Pb-SO_4)/Pb$				ΔE (mv)			
Pb=1	Pb=1	Pb=.2	Pb=.3	Pb=.5	Pb=1	Pb=.2	Pb=.3	Pb=.5
0.05	0.95	0.95	0.83		0.65	3.62	2.35	
0.10	0.90	0.50	0.67		1.33	8.73	5.04	
0.15	0.85	0.25	0.50		2.05	18	8.73	4.49
0.20	0.80		0.33	0.60	2.81		13.96	6.43
0.25	0.75		0.17	0.50	3.62		22.32	8.73
0.30	0.70			0.40	4.49			11.54
0.40	0.60			0.20	6.43			20.29
0.50	0.50				8.73			
0.60	0.40				11.54			
0.70	0.30				15.16			
0.80	0.20				20.27			
0.90	0.10				29.00			

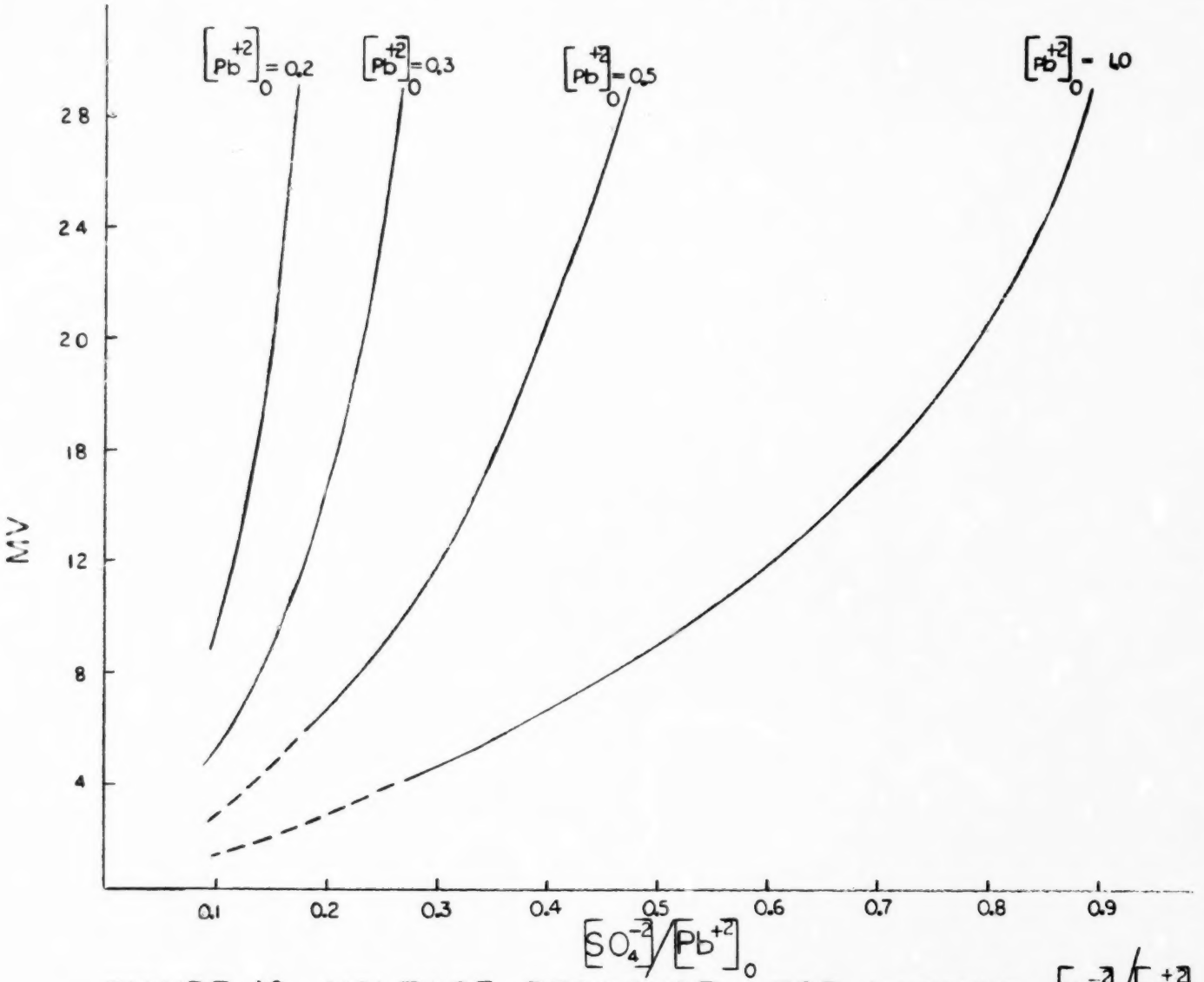

FIGURE 16 VOLTAGE RESPONSE FOR VARIOUS $[SO_4^{-2}]/[Pb^{+2}]_0$ RATIOS

$$\frac{dE}{d[SO_4]} = \frac{29}{2.3} \frac{1}{[Pb]_o - [SO_4]}$$

$$\frac{d[SO_4]}{dE} = 7.9\ ([Pb]_o - [SO_4])$$

This data is tabulated in Table XXVIII for 80% precipitation and for the maximum error points.

TABLE XXVIII

$[SO_4]/[Pb]_o$	$[Pb]_o$	$\frac{d[SO_4]}{dE(mv)\ [SO_4]} \times 100$ (% error/mv)
0.8	1.0	2%
0.5	1.0	8%
0.3	1.0	19%
0.2	0.5	12%
0.1	1.0	72%

We therefore decided to use the 0.1:0.3:1:3:10 increments of lead solutions.

E. SULFATE PROCEDURE DEVELOPMENT

An initial procedure was written in which the sulfate solutions were not premixed with an equal volume of methyl cellosolve acetate (MCA). The 50% MCA was maintained by having a higher MCA concentration initially (62.5%) which was diluted to 50% with the aqueous solutions. The blank was obtained by addition of water to the 62.5% MCA solution.

Initial results using this procedure were not as reproducible as had been obtained earlier. Hence a modified procedure was developed. The procedure uses the 0.1:0.3:1:3:10 lead ratios as described above.

This method is described in Appendix B.

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F. SULFATE SENSITIVITY BY STANDARD SUBTRACTION

1. Calculations of Voltage Response of Sulfate Addition

The above calculations (Section D) had neglected the dilution effect of the sulfate solution, and were based on 20 ml of $Pb(ClO_4)_2$. The calculated voltage shift for the sulfate additions used in the study to be described below are given in Table XXIX. In these tests, 10 ml of sulfate solution was added to 15 ml of lead solution. Since the ratios of Pb/SO_4 solutions remain constant, the calculations can be used at each lead level.

TABLE XXIX

VOLTAGE SHIFT FOR VARIOUS SULFATE INCREMENTS

ml (SO_4) *	$\frac{Pb}{(Pb\text{-}SO_4)\ V_1/V_2}$	mv Change
0	1.67	6.4
1.0	2.28	10.4
1.5	2.78	12.8
2.0	3.33	15.0
2.5	5.00	20.3
3.0	8.30	26.6
3.5	21.3	38.5

* Balance of 5 ml is water. Also, 5 ml of MCA is added.

2. Results of Sulfate Analysis

The sulfate procedure described in Appendix B was tested on sulfate standards. The experiment was performed on a random order design.

The data of the sulfate study are presented in Figures 17-20. It is evident that in many instances the experimental curves do not follow the theoretical curve. We believe this is due to an error in the equivalence of the

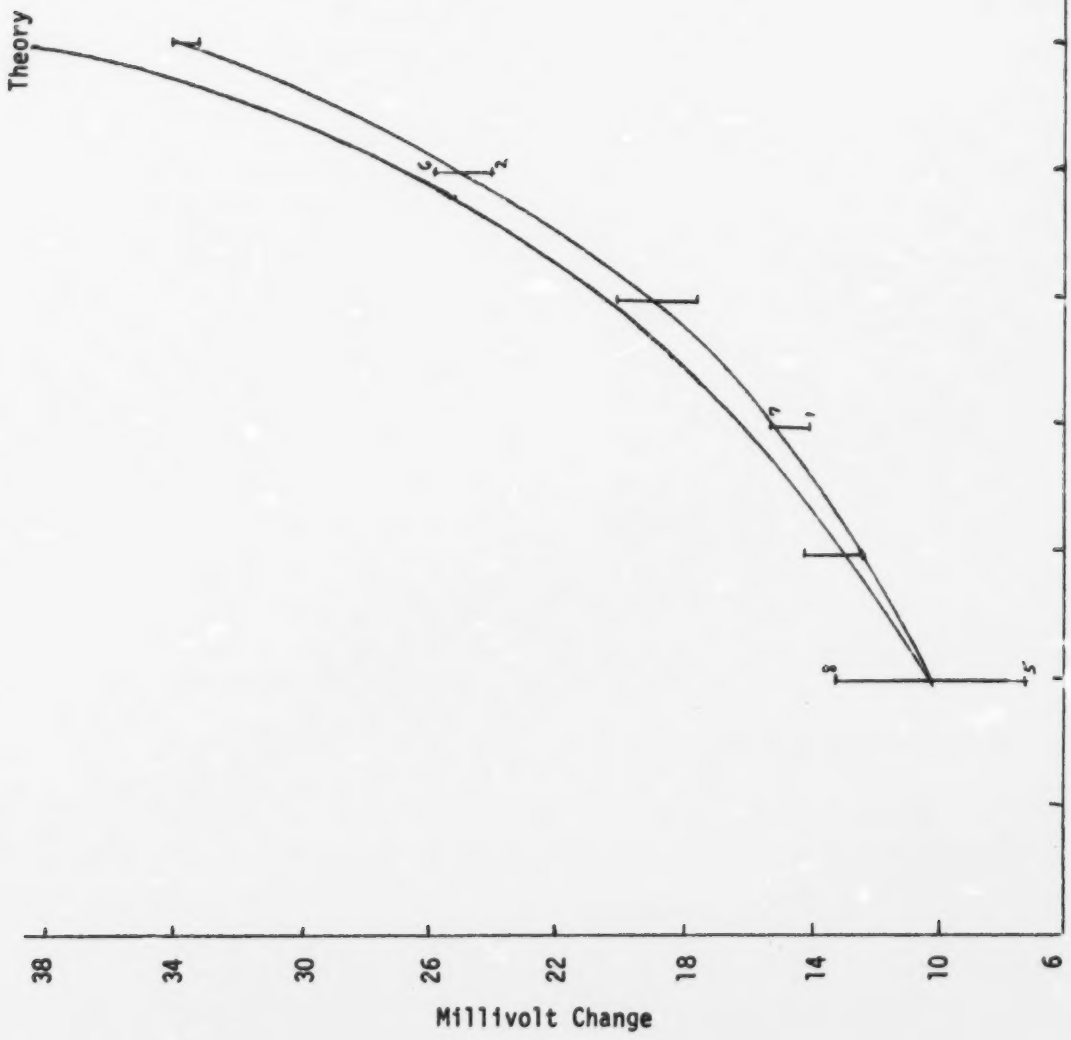

Figure 17. Addition of 4 x 10^{-4}M Na_2SO_4 Solution to 10^{-4} $Pb(ClO_4)_2$ Solution.

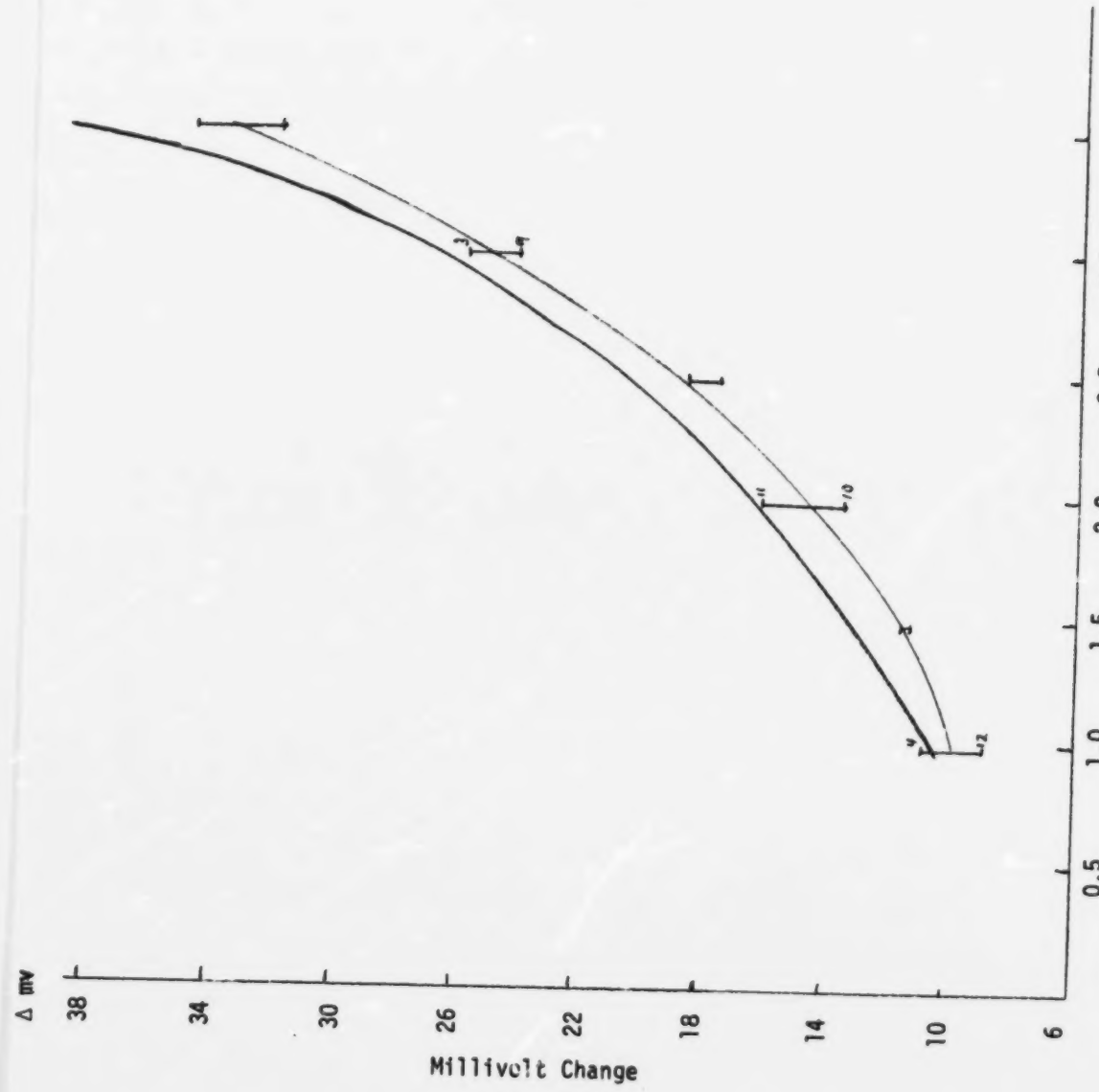

Figure 18. Addition of 1.2×10^{-3}M Na_2SO_4 Solution to 3×10^{-4}M $Pb(ClO_4)_2$ Solution.

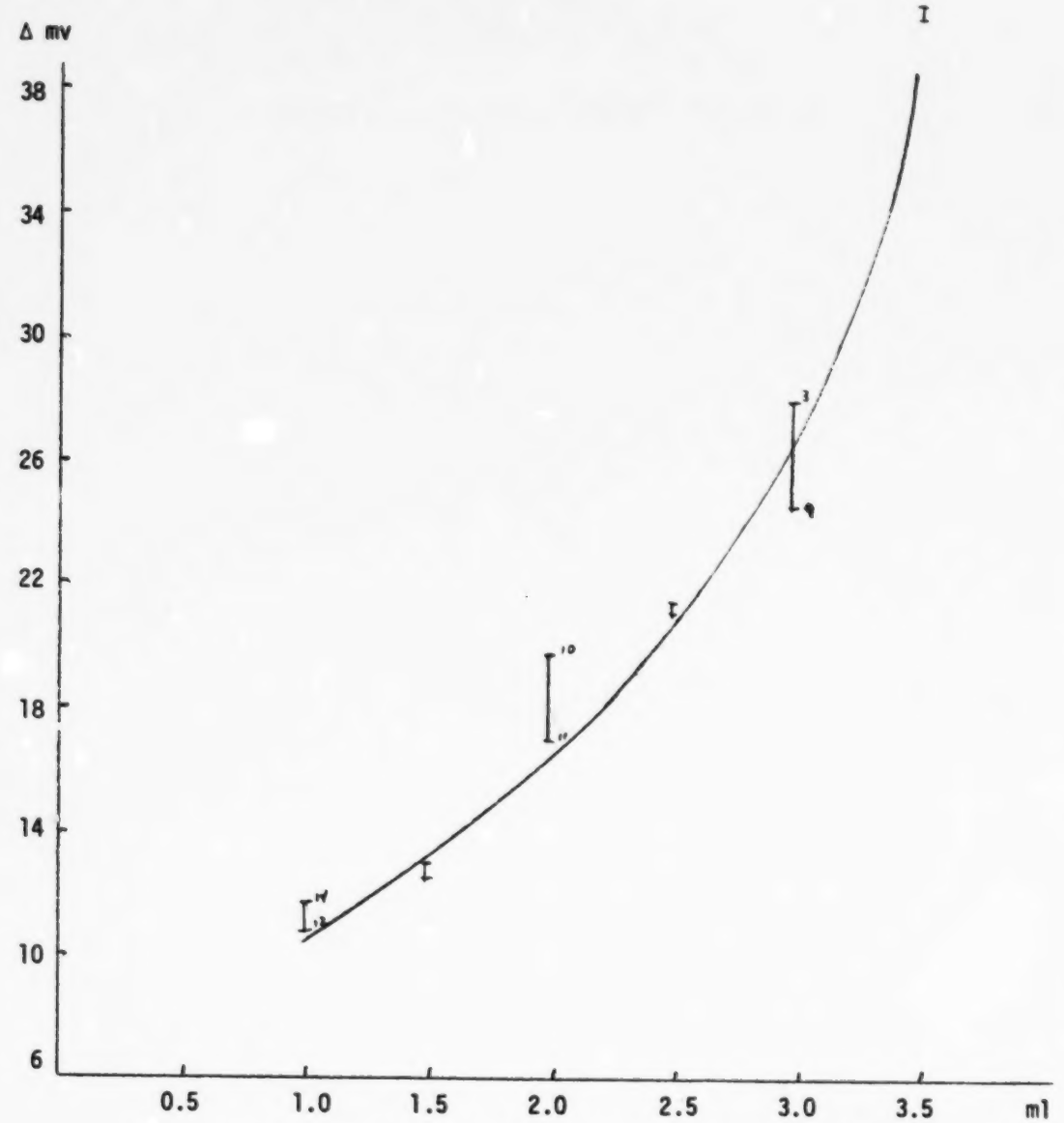

Figure 19. Addition of 4×10^{-3}M Na_2SO_4 Solution to 10^{-3}M $Pb(ClO_4)_2$ Solution.

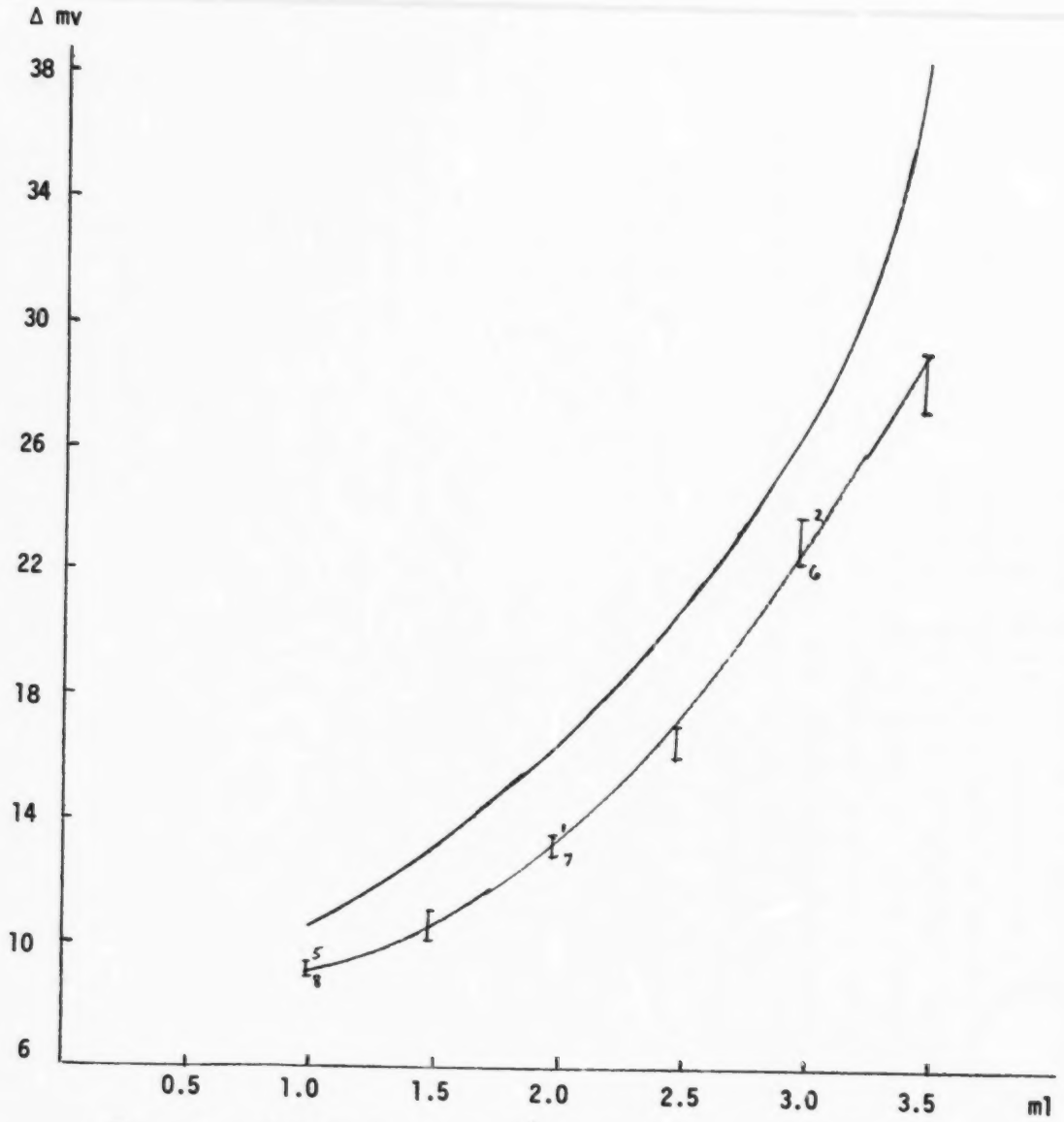

Figure 20. Addition of 1.2×10^{-2}M Na_2SO_4 Solution to 3×10^{-3}M $Pb(ClO_4)_2$ Solution.

lead and sulfate solutions. We anticipate that the theoretical curve can be used for calibration purposes when this problem is eliminated.

The experiment was performed in a random order. However, the experiments using 3.5, 2.5 and 1.5 ml of Na_2SO_4 solution were performed on days 1-2 and the 3.0, 2.0 and 1.0 ml quantities later, on days labeled day 3-4. The average difference in millivolts of the non-consecutive duplicates was 1.7 mv. This can be converted to a standard deviation of 1.49 mv (Moroney, 1956) for the method. The source of this error is analyzed in Table XXX. It is evident that the millivolt error is independent of the fraction of lead precipitated. Hence, the above analysis of the sulfate error, as a function of the millivolt error, is valid. There does appear to be a difference between day 1-2 and day 3-4. Also, the error at the low sulfate (lead) concentration is greater than at the higher concentration levels.

There is no effect of test order on abnormally high and low mv values. This was analyzed on days 3-4 and the number in Figures 17-20 refer to this test order.

TABLE XXX

EVALUATION OF SULFATE METHOD

		N	Range (mv)	S.D. (mv)
Day 1-2	3.5-2.5-1.5 ml	(12)	1.19±0.88	1.05
Day 3-4	3.0-2.0-1.0 ml	(12)	2.17±1.49	1.92
High frac.	3.5-3.0 ml	(8)	1.86±1.03	
Low frac.	1.0-1.5	(8)	1.64±1.86	
Medium	2.0-2.5	(8)	1.55±0.98	
Low conc.	4×10^{-4}M	(6)	2.40±1.81	2.13
Low conc.	1.2×10^{-3}M	(6)	1.75±1.01	1.55
Low conc.	4×10^{-3}M	(6)	1.42±1.39	1.26
High conc.	1.2×10^{-2}M	(6)	0.83±0.50	0.74
Overall		(24)	1.68±1.3	1.49

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G. GRAN'S PLOT PROCEDURE

The major problem with the standard subtraction method is the loss of sensitivity due to the larger volume of lead solution versus the unknown sulfate solution.

Another method, which might improve the precision, as well as increase the sensitivity of the analysis, is the use of Gran's plots to obtain a titration end point. In this method small volumes of increasingly concentrated Pb $(ClO_4)_2$ solutions would be added until excess lead is sensed. The system could then be adjusted to a standard volume and increments of the final Pb $(ClO_4)_2$ solution would be added. This method was simulated by calculating the response to an arbitrary random sulfate solution. The method and results are described below. We used the same solutions which would be required for the standard subtraction method.

In the simulated procedure, 9 ml of unknown (1.23×10^{-4}M equals 1.11μ moles sulfate) were placed in test vessel with 9 ml MCA, and the following solutions were added:

0.1 ml	1×10^{-4}M Pb $(ClO_4)_2$	+ 0.1 ml MCA	= 0.01μ moles added
"	3×10^{-4}M	"	= 0.04
"	1×10^{-3}M	"	= 0.14
"	3×10^{-3}M	"	= 0.44
"	1×10^{-2}M	"	= 1.44 = excess Pb^{++} indicated by voltage jump

Following this we assume addition of 0.5 ml H_2O + 0.5 ml MCA to bring volume to 20 ml. Read meter (e.g., 15.1 mv).

Add 0.1 ml of 1×10^{-2}M Pb $(ClO_4)_2$ + 0.1 ml MCA Read (e.g., 32.6 mv)
0.1 ml of 1×10^{-2}M Pb $(ClO_4)_2$ + 0.1 ml MCA Read (e.g., 39.6 mv)
0.1 ml of 1×10^{-2}M Pb $(ClO_4)_2$ + 0.1 ml MCA Read (e.g., 44.2 mv)
0.1 ml of 1×10^{-2}M Pb $(ClO_4)_2$ + 0.1 ml MCA Read (e.g., 47.3 mv)

Plot data on 10 percent volume corrected Gran's plot paper. Extrapolate to

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equivalence (0.067 ml - Figure 21) and add μ moles added of more dilute solutions (0.44 μ moles).

Calculate quantity

$$0.067 \text{ ml} \times 1 \times 10^{-2}\text{M} = 0.067 \text{ } \mu \text{ moles} + 0.44 \text{ } \mu \text{ moles} = 1.11 \text{ } \mu \text{ moles/9 ml}$$

In practice the error involved in extrapolating Gran's plots would be expected to be small compared to the back calculation from two points and a calculated slope (standard subtraction). Also the Gran's plot method eliminates a search for the correct lead solution. Simplification of the above procedure would be addition of 10 ml of unknown. The error in extrapolating 0.1 ml additions to 10.1 - 10.7 ml volumes, versus a 10 ml volume, is minimal on Gran's paper. The data calculated for 10.5 ml of solution above is also plotted on Figure 21. The extrapolated value showed no significant error.

H. GRAN'S PLOT EVALUATION

Twelve solutions of five different concentrations of Na_2SO_4 were analyzed using the procedure described above. Sulfate solutions between 1×10^{-5}M to 3×10^{-3}M were measured. The average percent error of these 12 analyses was 35%. Eliminating the 1×10^{-5}M concentration the error was 30%. These data are shown in Table XXXI (Series 1).

Since the Oxford pipette (0.2 ml, 50% unknown + 50% MCA) appeared sometimes to give false volumes the study was repeated at three concentrations using 20 times the volume and using glass pipettes. However the error remained about the same (24% average error, Series 2).

Hence we cannot recommend this method of analysis. Therefore the standard subtraction method described above was used for the analysis of high volume sample filters, since this method showed better precision on known samples.

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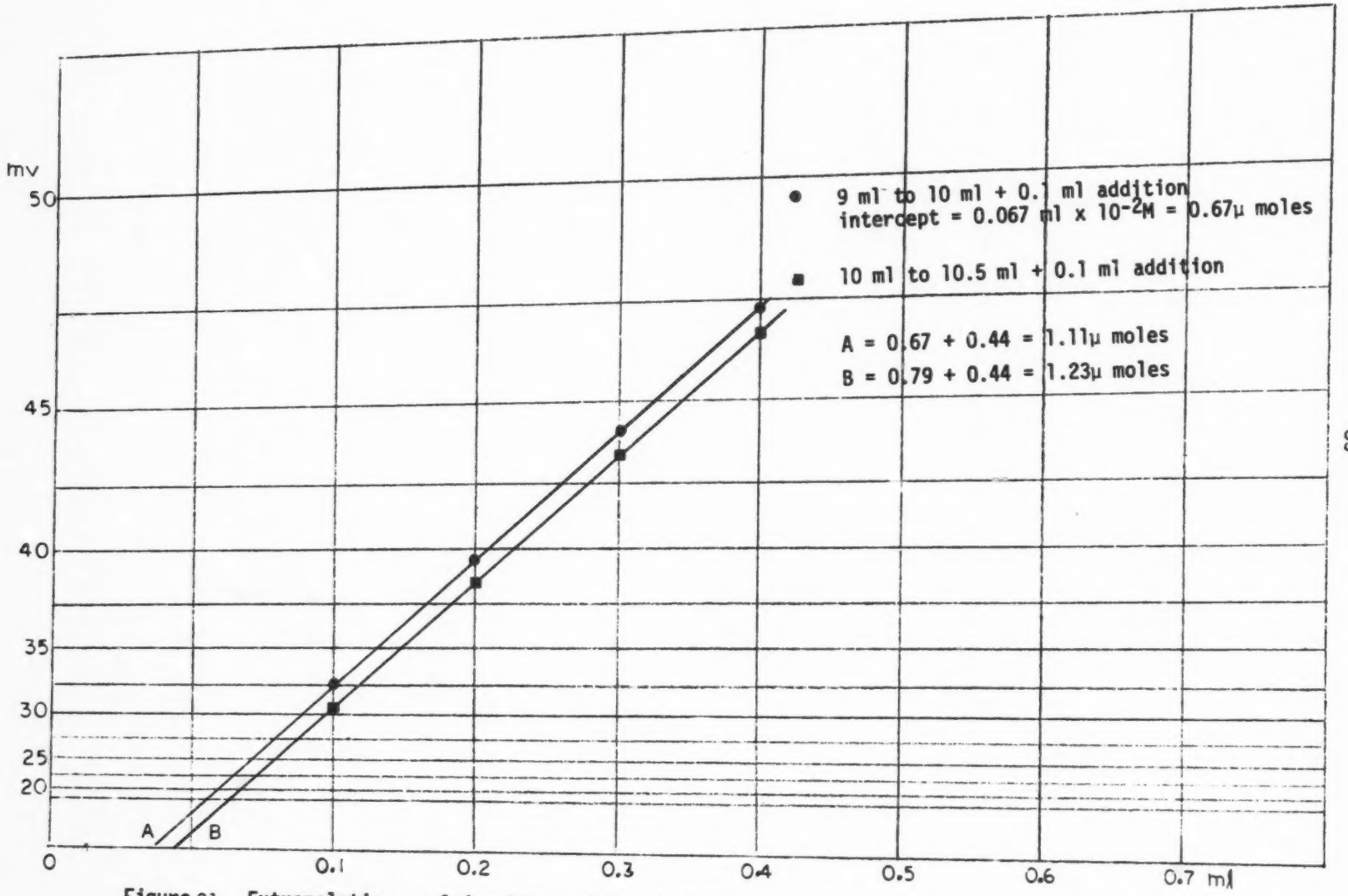

Figure 21. Extrapolation on Orion Research/Gran's Plot Paper (10% volume corrected) of Sulfate by Determining the Excess Lead (calculated values).

TABLE XXXI

EVALUATION OF GRAN'S PLOT METHOD FOR DETERMINING SULFATE IN KNOWN STANDARDS

Molar Concentration		% Error
Calculated	Observed	
Series 1: 10 ml total sample (0.1 ml unknown + 0.1 ml MCA, to 10 ml lead solution)		
$1x10^{-5}$	$1.6x10^{-5}$	+60
$1x10^{-5}$	$1.6x10^{-5}$	+60
$1x10^{-4}$	$7.0x10^{-5}$	-30
$1x10^{-4}$	$8.6x10^{-5}$	-14
$5x10^{-4}$	$3.5x10^{-4}$	-31
$5x10^{-4}$	$5.3x10^{-4}$	+6
$5x10^{-4}$	$6.3x10^{-4}$	+26
$1x10^{-3}$	$6.5x10^{-4}$	-35
$1x10^{-3}$	$6.1x10^{-4}$	-39
$1x10^{-3}$	$6.5x10^{-4}$	-35
$3x10^{-3}$	$1.5x10^{-3}$	-50
$3x10^{-3}$	$2.0x10^{-3}$	-35
Series 2: 50 ml total sample		
$5x10^{-5}$	$6.3x10^{-5}$	+26
$2.5x10^{-4}$	$3.3x10^{-4}$	+32
$5x10^{-4}$	$4.4x10^{-4}$	-13

I. SULFATE MEASUREMENT OF HIGH VOLUME FILTERS

Separate sections of filters described in Section V.G, labeled S-1 through S-9, were analyzed for sulfate by the electrode and barium chloranilate (Driscoll et. al., 1972) procedures. A 2.5 cm x 19 cm section of filter was used and the filtrate was diluted to 20 ml. This allowed both procedures to be run on the same extracted sample. However, it lowered the quantity of sulfate in each procedure by 50%. Three concentrations of $Pb(ClO_4)_2$ solution were required, and each concentration was titrated with sulfate to produce a standard curve. However the data indicated that this is not required.

The data are presented in Tables XXXII and XXXIII and Figure 22. It is probable that the filter blanks as determined by the barium chloranilate procedure are too high. We tend to believe the electrode blank determination. However there is also a discrepancy between the methods for S-7 and S-9. The electrode gives the higher value in these cases. However it is not known which method is correct. From an analysis of the sample locations, both filters came from Birmingham, Alabama. We believe that the error may be caused by metal ions which precipitate the chloranilate ions and generate low values for sulfate by this method. Al^{+++}, Ca^{++}, Fe^{+++}, Cu^{++} and Zn^{++} are known to interfere in this manner:

$$Ba\ Chl + SO_4^{=} \rightarrow BaSO_4 + Chl^{=} \quad (530\ nm\ color)$$

$$Chl^{=} + M^{++} \rightarrow M\ Chl$$

Adding a cation exchange step is reported to eliminate this problem. Alternately, we may be precipitating an anion with lead which is soluble with barium ion. This appears to be less likely, although solubilities of lead salts in 50% MCA are not known.

With these two exceptions we have obtained an excellent one-to-one correlation between the electrode and colorimetric methods. The percent standard deviation between the methods is 9.5% (Table XXXIV). This indicates that in general we are measuring total soluble sulfate in spite of adding 50% methyl cellosolve acetate.

TABLE XXXII

ELECTRODE DATA FOR HI VOL SULFATE MEASUREMENT

Sample	% of Extract	Initial Pb^{++} Molarity*	ΔE mv	% of Pb^{++} Precipitated
S-1	5	$3x10^{-4}$	13.4	44
S-2	5	$1x10^{-4}$	17.2	60
S-3	5	$1x10^{-4}$	15.4	54
S-4	5	$1x10^{-4}$	14.6	50
S-5	5	$1x10^{-4}$	16.9	59
S-6	5	$3x10^{-4}$	16.0	52
S-7	5	$1x10^{-4}$	12.9	45
S-8	5	$1x10^{-4}$	13.8	49
S-9	5	$3x10^{-4}$	13.8	46
Blank	25	$3x10^{-5}$	23	96
Blank	25	$3x10^{-5}$	18	85

* 15 ml of 50% MCA Solution

TABLE XXXIII

COMPARISON OF SULFATE ON HI VOL FILTERS BY ELECTRODE AND BARIUM CHLORANILATE METHODS

Sample	Sulfate Quantity ($\mu g/48\ cm^2$)	
	Electrode	Colorimetric
S-1	3800	3910
S-2	1710	2050
S-3	1570	1650
S-4	1440	1260
S-5	1690	1620
S-6	4490	4700
S-7	1300	552
S-8	1400	1560
S-9	3930	1760
Blank	164	628
Blank	140	1080

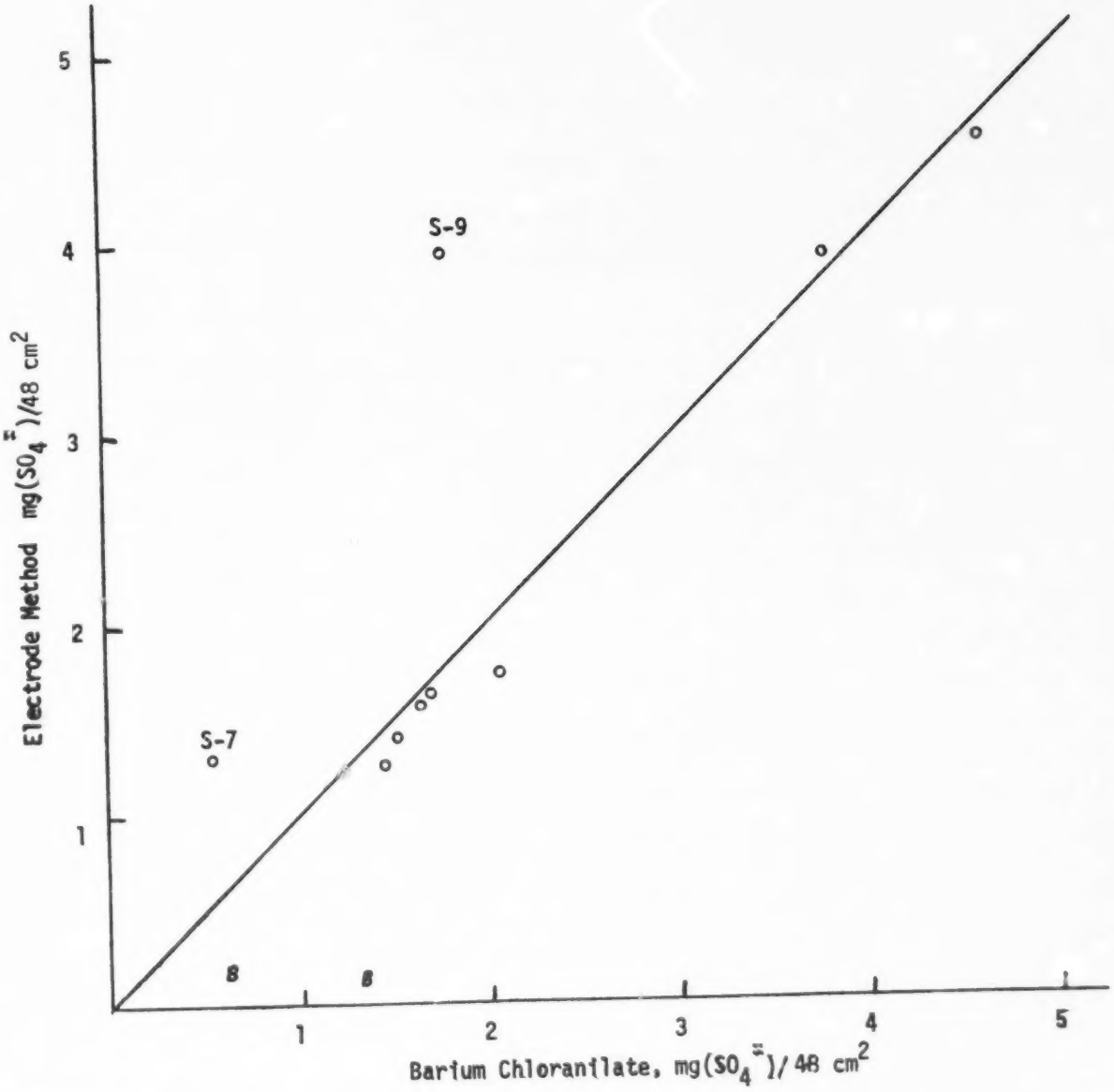

FIGURE 22. COMPARISON OF ELECTRODE AND COLORIMETRIC METHODS

TABLE XXXIV

CORRELATIONS OF SULFATE ANALYSIS

Data	Correlation Coefficient	Linear Regression y=electrode in mg x=Chloranilate in mg
all	0.82	$y = 0.805x + 665$
excluding S-7, S-9 and Blanks	0.992	$y = 0.945x + 0.039$

Std. Dev. $\simeq$ Ave. Dev. $\times \frac{2}{\sqrt{\pi}}$

Assumes: Electrode (y) = Colorimetric (x)

	Std. Dev. (mg)	% Std. Dev.
S-1 through S-9	510	27.0
Excluding S-7 and S-9	185	9.5

With the use of ultrasonic agitation in a test tube and use of an acid washed filter press the method is relatively simple. By use of a third of the required sample, and a preliminary electrode measurement, the range of the method may be expanded to a decade without loss of sensitivity. The final reading is taken after addition of more sample or solvent (see Procedure and Recommendations). This method will also indicate whether the sample is outside the decade range, by use of only a third of the normal sample.

Obviously the method could be made more precise by using a smaller range, with more lead standards. Also the method can be made more sensitive by decreasing the total volume. The present system uses 25 ml of solution. If the samples contain 1 mg or more sulfate however, increased sensitivity is not required.

Walden

APPENDIX A

RECOMMENDED PROCEDURE FOR NITRATE ANALYSIS

Preparation of Standards

1. One liter of KNO_3 solutions

   $1x10^{-5}M$, $3x10^{-5}M$, $1x10^{-4}M$, $3x10^{-4}M$, $1x10^{-3}M$

   using KNO_3 Baker Analyzed Reagent and deionized water.

2. Add 40 ml of $10^{-1}M$ AgF solution (Alpha Organics, Ventron, Beverly, Mass.) to each solution.

3. Store in brown polyethylene bottles.

Preparation of Samples

1. Cut 10% of the exposed area of Hi Vol filter. Handle the filter with gloves.
2. Place in 16 mm test tube.
3. Add 15 ml of H_2O.
4. Break sample with metal spatula.
5. Place in ultrasonic bath for 5 minutes.
6. Press out liquid using Filter/Sampler, Unichem P5190-6, Scientific Products, Evanston, Ill.
7. Transfer this sample into 50 ml Tri Pour Beaker.
8. Add 0.6 ml of 0.1M AgF.
9. Use same procedure for unused Hi Vol filter for blank determination.

Test Procedure

1. Place ~15 ml of each standard ($1x10^{-5}$M to $1x10^{-3}$M), sample, blank, etc., into 50 ml disposable beaker (Tri Pour, VWR).
2. Insert clean magnetic stirrer.
3. Stir to release air bubbles.
4. Insert Orion nitrate and fluoride electrode assembly.
5. Read Orion Model 701 meter on millivolt scale after 2 minutes.

Wash Procedure

1. After each determination wash the electrodes and stirrer and blot dry with a Kim-Wipe.

Calculations

Plot standard curve from 10^{-5} - 10^{-3} M KNO_3^- on semi-log paper. Read unknown concentration from eurve. Calculate mg from concentration mg = M x 930, and multiply by 10 for total mg on filter. Or calibrate ordinate of curve in required units.

APPENDIX B

RECOMMENDED PROCEDURE FOR SULFATE ANALYSIS

1. Solutions

a. Stock Solutions (in water)

1×10^{-2} m $Pb(ClO_4)_2$

3×10^{-4} m Na_2SO_4

9×10^{-4} m Na_2SO_4

3×10^{-3} m Na_2SO_4

9×10^{-3} m Na_2SO_4

b. $Pb(ClO_4)_2$ Solutions (prepared daily)

1×10^{-4} m $Pb(ClO_4)_2$ = 2 ml 10^{-2} m $Pb(ClO_4)_2$
+ 98 ml H_2O
+100 ml MCA

3×10^{-4} m $Pb(ClO_4)_2$ = 6 ml 10^{-2} m $Pb(ClO_4)_2$
+ 94 ml H_2O
+100 ml MCA

1×10^{-3} m $Pb(ClO_4)_2$ = 20 ml 10^{-2} m $Pb(ClO_4)_2$
+ 80 ml H_2O
+100 ml MCA

3×10^{-3} m $Pb(ClO_4)_2$ = 60 ml 10^{-2} m $Pb(ClO_4)_2$
+ 40 ml H_2O
+100 ml MCA

c. Na_2SO_4 Solutions (prepared as knowns for calibrations as necessary)

From each of the four Na_2SO_4 solutions prepare standards to precipitate 0.3, 0.5, 0.7 and 0.9 of Pb^{++}.

Thus for 15 ml of $1x10^{-4}$ m $Pb(ClO_4)_2$, prepare

4.5 ml of $3x10^{-4}$ m Na_2SO_4	+ 0.5 ml H_2O	+ 5 ml MCA
3.5 ml	1.5 ml	5 ml
2.5 ml	2.5 ml	5 ml
1.5 ml	3.5 ml	5 ml

For 15 ml of $3x10^{-4}$ m $Pb(ClO_4)_2$, prepare

4.5 ml of $9x10^{-4}$ m Na_2SO_4	+ 0.5 ml H_2)	+ 5 ml MCA
3.5 ml	1.5 ml	5 ml
2.5 ml	2.5 ml	5 ml
1.5 ml	3.5 ml	5 ml

For 15 ml of $1x10^{-3}$ m $Pb(ClO_4)_2$, prepare

4.5 ml of $3x10^{-3}$ m Na_2SO_4	+ 0.5 ml H_2O	+ 5 ml MCA
3.5 ml	1.5 ml	5 ml
2.5 ml	2.5 ml	5 ml
1.5 ml	3.5 ml	5 ml

For 15 ml of $3x10^{-3}$ m $Pb(ClO_4)_2$, prepare

4.5 ml of $9x10^{-3}$ m Na_2SO_4	+ 0.5 ml H_2O	+ 5 ml MCA
3.5 ml	1.5 ml	5 ml
2.5 ml	2.5 ml	5 ml
1.5 ml	3.5 ml	5 ml

2. Samples

Identical to nitrate, steps 1-6.

Take aliquot of filtrate and add an equal volume of MCA.

3. Test Procedure

97.

Pipette 15 ml of $Pb(ClO_4)_2$ solution into 50 ml Tri Pour beaker.

Insert clean magnetic stirrer.

Stir to release air bubbles.

Insert Orion lead and double junction reference electrodes.

Read meter (mv) after 2 minutes.

Add 10 ml of sample (5 ml sample + 5 ml MCA)*.

Read meter (mv) after 2 minutes.

If deflection <10 mv use less concentrated $Pb(ClO_4)_2$

If deflection >38 mv use more concentrated $Pb(ClO_4)_2$

d. Wash Procedure

Same as nitrate procedure.

e. Calculations

Standard curve(s) of ΔE vs sulfate as fraction of lead used.

* In the analysis of unknowns, 1 ml of solution was added and an addition of 4 ml water or 4 ml sample was based on this initial deflection.

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